from the positive ion which it has left, describing an orbit similar to a large atom, but not going to infinite separation. This type of energy level and wave function, the energy lying only slightly below the continuum so that it will be important only at low temperature, and the wave function being very extended so that it will have large diamagnetism, may well be important in the theory of superconductivity, as discussed in the following paper.

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The Nature of the Superconducting State. II

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The discrete levels of the electrons of a metal, lying below the continuum of levels predicted by the energy band theory, and interpreted in an earlier paper as leading to the superconducting state, have been further investigated, though a quantitative discussion in the general case is still impossible. The wave functions correspond to electrons which can wander for some distance through the metal, but are held to a finite region by forces of interaction with positive ions. Such wave functions will carry no current in the ordinary way, for they correspond to the correlation of an electron and a positive ion, and the two move together. On the other hand, being similar to large atoms, they have a large diamagnetism, and hence may perhaps lead to London's form of theory of superconductivity. In the second section, this possibility is discussed. It is shown, by reference to the ordinary theory of diamagnetism, that the two conventional types of theory, one for bound electrons, the other for free electrons, are treated in such different ways that one cannot in all cases interpolate between them. Instead, as wave functions become larger and larger, one can continue to treat them by the method appropriate to isolated atoms, until they become so large that the energy associated with the Larmor precession becomes comparable with the atomic energy. Then the properties change, and the method appropriate to free electrons gradually becomes correct. This limiting size depends on the magnetic field, or conversely the limiting magnetic field depends on the size. It is shown that to produce superconductivity the orbits must be of the order of magnitude of 137 atomic diameters, a not unreasonable figure with our model. Then the limiting magnetic field, above which the large diamagnetism or superconductivity would be expected to disappear, proves to be of the order of a few hundred gauss, or the order of magnitude of fields actually necessary to destroy superconductivity.

I. The Wave Functions

In an earlier paper, the author has suggested[1] that the electrons in the superconducting state may be in special stationary states of the system as a whole, lying a little below the lowest state as described by the Bloch theory of energy bands, and expressible only as a linear combination of Bloch functions, meaning that a certain correlation or cooperation between the electrons is necessary to bring this state about, which would be disturbed by temperature agitation. These special stationary states have now been further investigated, and in the present paper their nature is described in more detail, and it is shown that it is even more plausible than before that they may be really responsible for superconductivity. In the first section we discuss the nature of the wave functions and energy levels of the problem. The second section is devoted to showing that the wave functions are of the sort to be expected for superconductivity. London[2] has objected quite properly to the earlier paper, on the ground that superconductivity has much closer resemblance to diamagnetism than to ordinary conduction, a point of view which he has elaborated on previous occasions.[3] It is very

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[1] J. C. Slater, Phys. Rev. **51**, 195 (1937).

[2] F. London, Phys. Rev. **51**, 678 (1937).

[3] F. and H. London, Proc. Roy. Soc. **A149**, 71 (1935); Physica **2**, 341 (1935); F. London, Proc. Roy. Soc. **A152**, 24 (1935), and others. See particularly F. London, *Une Conception Nouvelle de la Supra-Conductibilité, Actualités Scientifiques et Industrielles* (Paris, 1937).

gratifying that the present theory has rather automatically developed along the lines of London's ideas, in that the special states previously described prove not to carry current in the ordinary way, but on the other hand prove to be just the sort capable of showing an extremely large diamagnetism.

It is now possible to discuss fairly completely the problem of a crystal containing two energy bands, each capable of holding N electrons, but one actually occupied by $N-1$, the other by one, electron.[4] We shall first describe the solution in nonmathematical language, hoping to understand its nature well enough so that we can indicate its extension to the actual problem in which a number of energy bands are partly occupied. This general problem is much too difficult to work with mathematically at the present time, and it is hard to see how the theory can be applied quantitatively to it without extreme complication, so that a qualitative discussion must suffice for the present.

At the outset it should be stated that we shall regard an energy band as a group of N levels, capable of holding N electrons per crystal of N atoms, of a given spin, and that we shall regard a group of N levels associated with one spin as being a different band from the group of N levels associated with the opposite spin. The essential point is that the one electron changing from one band to the other must change its atomic wave function, and it is immaterial to the general theory whether it changes the dependence of this atomic wave function on coordinates or on spin. It is for this reason that the ferromagnetic problem, where an electron reverses its spin but stays in the same band as far as orbital functions are concerned, is closely analogous to the optical absorption problem, where the electron changes its orbital function without change of spin. This observation shows that in the previous paper on superconductivity,[1] it was incorrect to suppose that the alkali metals, and copper, silver, and gold, are essentially different from other metals on account of having electrons in only one energy band. For they have electrons of both spins, and from the standpoint of the general theory that amounts to two bands, just as with other metals. In view of this fact, and of recent experimental work pointed out by Mendelssohn,[5] it seems unlikely that the theory in its present form is far enough advanced to predict which metals should show superconductivity and which should not. As we shall describe it, it certainly seems like a phenomenon which might be very widespread.

Let us call the almost filled band A, the almost empty one B. First consider the state where A is entirely filled, B entirely empty. Then the Pauli principle operates between all the N electrons in state A, in such a way as to prevent two of them from piling up on one atom at the same time. The result is an extraordinarily uniform charge distribution, quite without local fluctuations, except of course in going from one part of an atom to another. If we suppose that there are enough electrons just to neutralize the nuclei, this means a very constant electrical potential throughout the crystal. Whenever an electron moves from one atom to another, the Pauli principle demands that one move from the second atom back to the first. This shows us at once why no current can flow in such a state, since every motion of electricity is compensated by an equal and opposite motion.

Next imagine that one electron is removed from state A, placed in state B, and let us describe the situation in terms of energy bands, so that there is an empty level among the N states of band A, a filled level in band B. Of course, the lowest resulting energy, in the energy band theory, is found if the electron is removed from the highest state of band A, put in the lowest state of band B. We shall refer to the zero of energy throughout as the energy of the state where band A is filled, and we shall now consider the energy of this new state, which we shall call the excited state, referred to that zero. This excited state can be higher than the original state, in which case the system tends to have band A filled, band B empty, or it can be lower, in which case electrons tend to occupy both bands.

If the electron in band B is in a modulated wave function such as one has in a periodic lattice, that means that it is circulating freely through the crystal, and is as likely to be found

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[4] J. C. Slater and W. Shockley, Phys. Rev. 50, 705 (1936); G. Wannier, Phys. Rev. 52, 191 (1937); J. C. Slater, Phys. Rev. 52, 198 (1937).

[5] K. Mendelssohn, Phys. Rev. 51, 781 (1937).

on one atom as on another. This circulation is now permitted by the Pauli principle, for this electron no longer has the same atomic wave function as the other electrons, and can occupy an atom already holding another electron. But there is a price demanded for the privilege of free circulation. This price is the energy required for the electron to be removed from its original atom (essentially the ionization potential, as distorted by the existence of the lattice), minus the energy recovered when it forms a negative ion on another atom (the electron affinity of the neutral atom, again distorted by the lattice). If the electron is not removed to a very distant atom, this is diminished by a Coulomb term: as the negative ion is removed from the positive ion left behind, work must be done against the Coulomb attraction between the ions, so that the total work which we reckoned above, representing the work necessary to remove the ions to infinite separation, must be decreased if the separation is only finite. Now the actual excited electron is equally likely to be found on any atom of the crystal, so that there is only a negligible chance that it will be near the positive ion, and this Coulomb term can ordinarily be neglected. The price demanded for the formation of the excited state then is essentially an ionization potential minus an electron affinity, a matter of several volts. But in the cases we are interested in, it is worth the price, for we shall assume that the bottom of band B lies well below the top of band A, far enough below so that the gain in energy is more than the loss, and the excited state really lies below the normal one. If the excitation consists of reversal of spin, without change of orbital motion, this means that we are not dealing with a ferromagnetic system. If it consists of change from one band to another, it means that the second band B, though it may be higher than A, still overlaps it enough so that the bottom of B is decidedly below the top of A. We find in either of these cases that the lowest state, in the language of energy bands, is that in which the excited electron is essentially at rest at the bottom of band B, the hole in band A being at the top of that band, and therefore again essentially at rest (since the slope of the energy *vs.* k curve gives the velocity, and this is zero both at the maximum and minimum energies). But these ions are both distributed with equal probability on each atom of the system, so that they have no relation to each other.

The state which we have thus derived is one in which there is a fluctuation of charge distribution. The positive and negative ions are equally likely to be found anywhere within the crystal. There is no longer the uniformity of charge and potential found in the normal state. Now a nonuniform charge distribution results in an increased potential energy. This can be seen from the fundamental principles of electrostatics. The electrostatic, potential energy can be written as $(\frac{1}{8}\pi)\int E^2 d\tau$, reducing to zero in a uniform potential where E is zero, but increasing wherever there are nonuniformities of potential. It is this increase of potential energy which we have described as the price which must be paid in order to excite an electron. We now ask, have we perhaps paid too great a price? Could we have set up some other state, with less fluctuation of charge density and potential, which would have had an even lower energy? To have less fluctuation, we must correlate the motions of positive and negative ions, arranging the state so that the chances are large that they will be found close together, small that they will be far apart. This can be done by building up a wave packet of excited states of the form we have used, each corresponding to an electron removed from one level of band A, and placed in one level of band B. If we wish to go to an extreme, we can arrange the packet so that the negative and positive ions are practically sure to coincide, and we have to pay no price at all for our excitation in the matter of potential energy. But we have a compensating loss in other energy, for it turns out that to make such a packet we must use all possible excited states, with equal coefficients, amounting to removing the electron from a mean position in band A, placing it in a mean position in band B, instead of going from the top of A to the bottom of B. In the particular case of ferromagnetism, bands A and B coincide in energy, so that in some cases it can turn out that the resulting loss of energy is very small. But if band B lies above A, the loss of energy would be considerable, and this state would probably have about as high an energy as the energy band state, or even much higher.

The situation we have just described can be looked at in a more graphic way. If the electron in band B practically coincides with the hole in band A, its wave function must decrease very rapidly as it leaves the hole. This rapid decrease, perhaps of an exponential sort, means a large kinetic energy. In other words, the increase of kinetic energy associated with such a concentrated packet more than makes up for the decrease of potential energy, in most cases. To get the really lowest energy, we must make a compromise. We build a more extended packet, so that the positive and negative ions may be found at a distance of a good many atomic diameters, but still will not wander to infinite separation from each other. This will not decrease the potential energy so much as before, but neither will it give a function that varies as much with position, so that the kinetic energy will not be as much increased. The resulting wave function can be looked at in a very physical way. Both electron and positive hole are capable of moving through the crystal (the hole "moving" by the shift of neighboring electrons into the hole, leaving a new hole on the neighboring atom). Each has a certain "effective mass," as found in the usual theory of metals, determined by the curvature of the energy-momentum curve. There is a potential energy of interaction between them. Then the wave function is approximated by that of a two-body problem with the effective masses and potential energy just described. Such a two-body problem would be similar to a hydrogen atom, except that both positive and negative particles are mobile. It has many energy levels and wave functions, the wave functions getting more and more extended as we pass to the limiting continuum at the limit of the series, and the energy levels getting closer and closer together. The levels considered in the conventional theory are simply the continuum of levels beyond the series limit, in which the electron and hole independently wander through the crystal. The discrete stationary states correspond to the discrete energy levels of a two-body problem.

This elementary picture gives one definite piece of information about these discrete wave functions: they cannot carry current in the ordinary way. For if such a function moves bodily through the crystal, both the electron and the hole move with the same rate, corresponding to equal transports of negative and positive electricity, which just cancel. Thus the existence of such levels cannot lead to a theory of enhanced ordinary conduction, as was suggested in the earlier paper.[1] In fact, if many electrons of the metal went into such states, the ordinary conductivity would be decreased, not increased.

On the other hand, there is another property of these wave functions which is just what is needed to produce a large diamagnetism. In most actual cases, the wave functions will presumably be quite extended, allowing the positive and negative charges to wander to a considerable distance from each other. That is, they will be analogous to large "atoms," much larger than ordinary atoms, but small compared to the crystal as a whole. Now the diamagnetic susceptibility of an atom is proportional to the square of its radius. Thus wave functions of this type, having a large radius, can correspond to very large diamagnetism, and can lead to London's theory of superconductivity. This is discussed in the second section.

The discussion so far has been concerned with the case in which one electron only was in band B, the remaining $N-1$ electrons being in band A. Actually, most metals have a number of bands simultaneously occupied by electrons. If the metal is not ferromagnetic, each band of one spin will be accompanied by the corresponding band of the opposite spin, and each will be equally occupied. Furthermore, practically all metals except the alkalies, copper, silver, and gold have at least two different energy bands partly occupied. The resulting problem would be extremely involved to treat in detail, and we shall not try it. But we can see qualitatively what will happen. If we set up the lowest level according to the theory of energy bands, with a number of partly occupied bands, there can be large fluctuations in the charge on each atom, for an electron corresponding to any one of the bands can be present or absent on an atom, independently of the others. Thus, as before, this state will correspond to considerable fluctuations of the potential from point to point, and to a considerable potential energy. In an effort to reduce this fluctuation, there will be special states into which each of the electrons can fall, localized near the minima of potential energy, with energies slightly lower than those of the continuum. We can imagine a crude method of successive approximations by which these levels might be found. We could start with the energy band function. A particular, typical arrangement of electrons in it would correspond to a certain fluctuating charge distribution, with certain minima and maxima of potential. We could imagine all the electrons but one frozen in these particular positions, and let the remaining one move in the resulting field. It would have possible wave functions concentrated near the minima of potential energy, avoiding the maxima. Having found these functions, we could set up a new approximation, by putting the electrons in the lowest functions of this type, instead of in the energy band states. We should presumably find that the potential in this case had been overcorrected, and a repetition of the same process would result in more extended functions as a next approximation, and so on. Whether such an approximation would actually converge is a question, and it certainly would not be practical for computation, but it suggests a possible state of the system as a whole in which many or most of the electrons would have wave functions which were damped off in space instead of extending through the whole crystal.

This type of calculation reminds one of that made by Wigner and Seitz[6] in discussing correlation energy in a crystal. There they considered particularly the way in which the wave function of one electron kept out of the immediate neighborhood of another electron. They found that by setting up wave functions in which this was accomplished, a very considerable gain in energy can be secured. Surely this calculation of Wigner and Seitz accounts for the larger part of the gain in energy which can be secured by electron correlation, and of course this is such a large energy gain that it is not affected by temperature. The small scale fluctuations in potential will be almost entirely ironed out by this small scale correlation, and the only fluctuations which may be supposed to remain will be rather long scale fluctuations of small amplitude. These will result in only a slight excess of potential energy, so that no great energy gain will result from removing them. Nevertheless it seems reasonable to suppose that states are possible in which these large scale fluctuations are largely ironed out as well, resulting in a still further slight energy gain. In such states, the wave functions of the electrons would show large scale modulation, again resembling the large "atoms" of our earlier picture of one excited electron, though we can no longer think of a single electron and hole as being correlated, but rather of an electron being correlated with a region of slight net positive charge. To make any significant energy gain by combining such functions, we should have to arrange them all in a very accurate way, just balancing charges so as to neutralize the potential fluctuations. This would mean that such a state would be one demanding large scale cooperation of the electrons, so that it would have analogies to other cooperative phenomena such as ferromagnetism and the formation of superlattices. We should expect, then, that such a state would be realized only at low temperatures, and that there would be a sharp transition point between it and the ordinary state of the metal, as is characteristic of the transition from ordered to disordered states.

We arrive, then, at a picture of the ordinary state as one in which the electrons move more or less freely through the metal, but modifying their wave functions in the way described by Wigner and Seitz when two electrons happen to come close together, so as to remove small scale fluctuations of potential, the ones which contribute most to the excess potential energy. At lower temperatures, a different phase would come in, in which the remaining large scale fluctuations would be largely removed, by replacing the wave functions by others which, rather than extending through the crystal, are damped off in a certain finite distance, and arranging the electrons in these functions in such a way as to reduce fluctuations as far as possible. This picture is unfortunately very vague, and it seems difficult to make it less so. In particular, we cannot calculate with any degree of accuracy the energy difference between the two types of states, or the size of the wave functions in the correlated state. The energy difference certainly must be small, compared with the ordinary correlation energy,

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[6] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934); E. Wigner, Phys. Rev. **46**, 1002 (1934).

and the wave functions large compared with the size of an ordinary atom. Our suggestion is that this correlated state corresponds to the superconducting state. If that is the case, the energy difference must be of the order of magnitude of kT for a few degrees absolute. And we shall show in the next section that the wave functions must be of the order of magnitude of several hundred atom diameters, on the average. We shall not attempt to show that the model actually leads to such figures, though of course it is to be noted that the change from wave functions modulated on a large scale, to those extending through the crystal, will be accompanied by a smaller and smaller energy change, the larger the range of the modulation is.

2. The Superconducting Property

In this section we shall largely free ourselves from the details of our model, and ask a definite question: Is it possible to have wave functions, falling off in a certain distance so as to act like big "atoms," which would show the superconducting property? At first sight, we may think of the theory of diamagnetism of single atoms, in which the diamagnetic susceptibility increases proportionally to the square of the radius. By making the radius as large as we please, we can increase the diamagnetism to any desired extent. London's[3] theory corresponds in most, though not quite all, details to the supposition that a superconductor is a substance with magnetic susceptibility $\chi=-\frac{1}{4}\pi$, so that $B=0$ inside the material. (As London points out in the references above, this is not a very accurate description, but it can serve for the moment in determining orders of magnitude.) Let us see how large the atoms would have to be to achieve this amount of diamagnetism. If there are N diamagnetic electrons per unit volume, each with a mean square radius $[r^2]_{\text{Av}}$, the theory of the diamagnetism of separate atoms gives $\chi=-e^2[r^2]_{\text{Av}}N/6mc^2$, where e, m, c have their usual meanings. We equate this figure to $-\frac{1}{4}\pi$. Further, we let $N=1/d^3$, where d is the side of a cube containing one diamagnetic electron. We shall assume this to be of the order of magnitude of interatomic distances, so that there is essentially one such electron per atom. Then an elementary calculation gives

$$([r^2]_{\text{Av}}/d^2)^{\frac{1}{2}}=137(3d/2\pi a_0)^{\frac{1}{2}}, \qquad (1)$$

where a_0 is the atomic unit of distance. If d is of the order of interatomic distances, $(3d/2\pi a_0)^{\frac{1}{2}}$ will be of the order of unity. Hence to get enough diamagnetism to agree with London's theory, the wave functions of our large "atoms" would have to be of the order of magnitude of 137 times an ordinary interatomic distance. And yet we should have to have as many electrons per atom as usual, so that these electronic functions would have to overlap a great deal. This is not inconsistent, as a simple model will show.

Let us suppose that the electrons were entirely free, but that the box containing them was divided into a set of cubic cells by impenetrable walls. We imagine these cells to have sides of the order of 137 atomic diameters, and assume that there are enough electrons per unit volume so that there are of the order of $(137)^3$ electrons in each cell. Then all the wave functions will decrease to zero at the edge of the cell, so that they will fall off in such a way as we have described. The energy levels of electrons in such a cell would be similar to those given by the ordinary theory of free electrons in a metal, and the lowest $(137)^3$ of these levels would be occupied by the electrons, each extending throughout the cell. Thus we should have the same number of electrons per unit volume as before, but with wave functions falling off in a distance of the desired order, many electrons occupying the same region. With the radius 137 times that of an atom, the diamagnetism could be of the order of $(137)^2$ times as great, which is roughly what is required to produce the complete diamagnetism of London's theory. The energy levels, furthermore, are now discrete. The total width of the occupied levels will be very closely the same as in the absence of the barriers, or of the order of a few volts. The energy difference between levels will then be of the order of a few volts divided by $(137)^3$, or the order of 10^{-6} volts, a very small energy difference, of the order of magnitude of kT for 0.01° Abs. Hence we may expect the temperatures required to produce changes in this state to be correspondingly low. It thus seems possible by a simple model to secure something like London's theory, and this model has essential points in common with that to which our theory of the metal has led us.

A difficulty will at once occur to the reader. It is not plain from this argument why we could not let the size of our cells increase, from 137 atom diameters, to any desired size. Then the diamagnetic susceptibility should increase without limit, as $[r^2]_{\text{Av}}$ continues to increase. And yet the model would approach the ordinary case of free electrons, from which we know by the work of Landau[7] that the diamagnetism has a very small value. We shall now consider this paradox, and show that our model is in fact consistent with the usual theory, and that there are points in connection with this theory which have not previously been brought out. What we shall do essentially is to consider the problem of N free electrons in a box, in which we vary the size of the box from a very small size, of atomic dimensions, through our size of the order of 137 atomic dimensions, to the whole size of an ordinary crystal, keeping the number of free electrons per unit volume (rather than the total number of free electrons) approximately constant. Then the energy separation of the levels will be of the order of a few volts divided by N, giving a few volts for a box as small as an atom ($N=1$), something like 10^{-6} for the box of the order of 137 atoms, as we have seen, and something like 10^{-23} volts for a whole crystal.

We shall consider first the two limiting cases of the single atoms and the entire crystal. The first is essentially the case of isolated atoms, or of the diamagnetism of bound electrons as treated by Peierls.[8] The second is the case of free electrons as treated by Landau.[7] In both cases the diamagnetism is small, and the methods used for treating them are similar in some respects. Hence it has been assumed naturally that one could interpolate between them, and that there was no place for large diamagnetism in the theory. We shall find that this view is erroneous, that the treatments of the two cases are essentially different, and that we make no error in supposing a large diamagnetism in our case of $N=(137)^3$.

Assume that a magnetic field is present, given by $\mathbf{H}=\text{curl }\mathbf{A}$, where $\mathbf{A}$ is a divergenceless vector potential. Then the relation between velocity $\mathbf{v}$ and momentum $\mathbf{p}$ is

$$m\mathbf{v}=\mathbf{p}-(e/c)\mathbf{A}=-(h/2\pi i)\nabla-(e/c)\mathbf{A}, \qquad (2)$$

the second equation representing the operator form. In this case Schrödinger's equation $(\frac{1}{2}mv^2+V)\psi=E\psi$ becomes

$$\left\{-\frac{h^2}{8\pi^2 m}\nabla^2-\frac{ieh}{2\pi mc}\mathbf{A}\cdot\nabla+\frac{e^2A^2}{2mc^2}+V-E\right\}\psi=0. \qquad (3)$$

For a constant magnetic field of magnitude H in the z direction, we can set $A_x=-Hy/2$, $A_y=Hx/2$, $A_z=0$, giving lines of $\mathbf{A}$ circulating around the z axis. Then Eq. (3) becomes

$$\left\{-\frac{h^2}{8\pi^2 m}\nabla^2-\frac{ieh}{4\pi mc}H\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)+\frac{e^2}{8mc^2}H^2(x^2+y^2)+V-E\right\}\psi=0. \qquad (4)$$

For a wave function possessing no permanent magnetic moment, the second term, proportional to H, vanishes, so that since we are not considering paramagnetism we can leave it out of account. The effect of the magnetic field, then, is to add the term in H^2. This has quite different results in the two limiting cases we are considering.

For a single atom, or a box so small as to contain only one atom, the term $(e^2/8mc^2)H^2(x^2+y^2)$ is negligible for any magnetic field at our disposal. It is convenient to express in terms of atomic units. We measure distances in terms of the radius a_0 of the first Bohr orbit, energies in terms of the Rydberg energy. The natural unit of H is that magnetic field for which $(eh/2mc)H$, or the energy of a Bohr magneton in that magnetic field, equals the Rydberg energy. This of course is an enormous magnetic field, and turns out to be approximately 3.8×10^8 gauss. In these units, the term is $\frac{1}{4}H^2(x^2+y^2)$. Then if x^2+y^2 is of the order of unity, and H of the order of 40,000 gauss, or 10^{-4} atomic units, this term in the energy is of the order of 10^{-8} atomic units, entirely negligible compared with the energy of an atom. Thus the term can be neglected in the wave equation, and we can determine the wave function by the original wave equation, so that to the first order there is no perturbation in the wave function produced by the magnetic field. This is the analog in wave mechanics to the Larmor theorem in classical mechanics. The change in energy in the magnetic field is then to be found from the

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

[8] R. Peierls, Zeits. f. Physik **80**, 763; **81**, 186 (1933).

average of the perturbation energy $\frac{1}{4}H^2(x^2+y^2)$ over the unperturbed orbit, and is thus proportional to H^2 (as is proper for diamagnetism) and to the mean square radius of the orbit. This is the basis of the ordinary theory of diamagnetism of atoms.

The situation is reversed in the case of free electrons in a box of the order of magnitude of the size of real crystals. In this case, the maximum x in the box will be of the order of 10^8 atomic units, so that if H is of the order of 40,000 gauss the magnetic energy will be of the order of 10^8 atomic units at the edge, an enormous value. In this case, in other words, the magnetic field furnishes a potential in which the electron must move, and the wave functions to a first approximation must be determined in this potential, and are different from those of free electrons. As is well known in the Landau solution, the corresponding wave functions resemble those of linear oscillators surrounding $x=y=0$ in the xy plane, falling off exponentially as the coordinates depart from these values, but are periodic with respect to z. This corresponds physically to the classical motion of the electrons, in which the z component is unaffected by the field, but the electrons spiral around the z axis, executing a periodic motion in the xy plane, which must be quantized in the quantum theory. For a given value of the z component of momentum, this quantization leads to an energy $2H(n+\frac{1}{2})$, where n is an integer, associated with the xy motion, in these units. In this case, the wave functions are changed in the first order by the presence of the magnetic field. It is then a complicated process to find the change in the energy of the whole system with the magnetic field. As the field changes, electrons have transitions from one energy level to another, and when the whole calculation is made, Landau's formula for diamagnetism of free electrons is found.

It is clear that the theories in these two cases are very different in nature. Now let us ask, what happens in the intermediate cases? If we let our box increase in size from atomic size, at what point must we begin to consider the first order effect of the field on the wave function? Up to this point we are allowed to use the atomic formula for diamagnetism, and the diamagnetism per electron will increase proportionally to the square of the dimension of the box. We shall not set up and solve this problem, though it should not be impossibly hard to handle it. But we can easily find the qualitative criterion to apply. It certainly seems most probable that if the spacing of levels as determined by the magnetic term in the potential energy (namely $2H$, in atomic units), is small compared to the spacing of the unperturbed levels (of the order of $1/N$, in atomic units), then we may use the unperturbed wave functions, and we have the atomic formula for diamagnetism. On the other hand, if $2H$ is large compared with $1/N$, we must find the new wave functions, treating the magnetic field as the principal term in the potential, and we shall get something much more like the free electron theory.

It is instructive to consider the variation, not with N at fixed H, but with H at fixed N. For any size box, and small enough magnetic field, the whole box will act like a big diamagnetic atom, but as the magnetic field increases a point will be reached where this is no longer true. Without a complete solution we cannot say exactly how the energy will act as function of H. In the region where the atomic formula holds, the energy will increase quadratically with H. When the formula breaks down it will presumably still increase, but much more slowly, so that the slope of the curve of energy against H, which gives the magnetic moment, will not only not increase proportionally with H, but may perhaps even decrease. As much larger fields are reached, the curve will approach another parabolic curve, with much smaller coefficient, corresponding to free electron diamagnetism. Physically, it is clear what is happening. At low fields, the Larmor precession is slow enough so that its frequency is negligible compared with the frequency of oscillation of an electron from one side of the box to another, its energy small compared to the energy difference between electrons. In particular, the term $\frac{1}{4}H^2(x^2+y^2)$ represents the increased kinetic energy on account of the Larmor precession, and this is negligible. At high fields, however, this added kinetic energy becomes large compared with the energy already present, and the whole motion is profoundly affected by the magnetic field. It is affected in such a way that the energy does not increase nearly as fast as the atomic picture would indicate. This occurs by having the various electrons move in orbits much smaller than the box as a whole, either in the spirals of free electrons, or surrounding the atomic nuclei in a real crystal, each orbit executing its own Larmor precession about its center. As a result, no part of the electron's path acquires a great enough velocity from the precession to add greatly to the kinetic energy.

The question now becomes, if N is of the order of $(137)^3$, what is the order of magnitude of the magnetic field necessary to destroy the highly diamagnetic state? In this case, the spacing of levels is of the order of magnitude of $1/N=4\times10^{-7}$ atomic units. To get the maximum value of x^2+y^2, we may assume the interatomic distance to be about five atomic units (about 2.5A), so that with a radius of the cell of the order of 137 (5)/2, we could have x^2+y^2 up to about $(137)^2\ 25/4=1.2\times10^5$. Then if we let $\frac{1}{4}H^2(x^2+y^2)=1/N$, we have $H=3.6\times10^{-6}$ atomic units $=1400$ gauss. This very crude calculation, in other words, has given us a critical magnetic field of the order of magnitude of the fields actually observed to destroy superconductivity; it is obvious that in such a rough calculation a factor of ten can be disregarded.

We are finally led to this very significant result, then. If we assume large wave functions for electrons in a superconducting body, which become occupied at low temperature in the superconducting state, then the theory of diamagnetism as applied to them will predict that they should be perfectly diamagnetic, which London's theory has shown to be essentially equivalent to superconductivity. The theory predicts, however, that this should hold only for low magnetic fields. And the order of magnitude of the limiting field calculated in this way agrees in a rough way with that actually found to destroy superconductivity.

Of course, it is obvious that the electrons will not all really have orbits of the same size. Some will be smaller than the size necessary to produce perfect diamagnetism, some bigger. We cannot expect the theory to lead to orbits just the right size, except by coincidence. But it will do no serious harm if they are somewhat too big, for diamagnetism can clearly not be carried beyond the point where the magnetic field within the crystal is completely cancelled by the induced currents. If the orbits were somewhat bigger than we have calculated, on the average, the effect would be to produce the transition at a lower critical magnetic field, more nearly the experimental situation. Also it is to be noted that the type of theory we have spoken of here would not lead to a sudden change of properties with increasing field, but instead to a gradual transition. We cannot expect to understand the sudden change except by combining these magnetic considerations with a real long-scale cooperative theory, for it is only in this way that sharp transitions can be explained. This would have to be done in a more elaborate theory.

Finally, to make the discussion more intelligible, we should point out, as London has done, the way in which the current appears in this form of theory. Eq. (2) for the velocity has a term $-(e/mc)A$, which is not present when the magnetic field is absent. This term appears in the presence of the field without any change in the wave function. Thus in our case of low fields, where the wave function is unchanged, there will be a term in the current, proportional to the magnetic field. In a uniform field, A circulates about the axis of the field, so that this additional current will do the same. The current thus produced is $-(e^2/mc)\psi^*\psi A$, a constant times A, which is London's fundamental equation. It is then clear that the resulting current produces a magnetic moment of the sample as a whole. More complicated cases will not be discussed in detail, for London has fully treated the consequences of this type of current. As London has pointed out, a current produced in this way by the magnetic field is not subject to dissipation by interaction with the lattice, so that this conduction is of essentially a different nature from ordinary conduction, and is not subject to resistance of the ordinary sort at all.

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