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The Nature of the Superconducting State

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It is tentatively suggested that the superconducting state of metallic electrons may arise by application of perturbation theory to Bloch's theory. The excited states of a metal, on the usual theory, form a continuum whose lower boundary is the normal state. It is shown that under some circumstances there are nondiagonal matrix components of energy between states of this continuum, which would tend to depress a few of the lowest states below their normal positions. These special states of the metal would resemble a thermodynamic phase, stable only at the lowest temperatures, and having practically zero entropy, in agreement with present theories of the thermodynamics of superconductivity. They would also tend to have extremely low resistance, on account of the small concentration of energy levels per unit energy range. It is therefore suggested that these states may constitute the superconducting state. It is shown that superconductivity is not to be expected for the alkalies, or for Cu, Ag or Au; and that it is to be expected only at extremely small temperatures for transition metals, as W, Fe, Ni, Pt; thereby accounting for most of the metals which are known not to be superconducting at temperatures so far attained.

THE electron theory of metals has developed far enough so that it ought to be possible to explain superconductivity. And the study of the superconducting state itself has progressed, both experimentally and theoretically, so far that its explanation should not be too difficult.[1] The present paper does not present a complete theory of the superconducting state, but it does indicate a point in the electron theory, so far not explored, where we may very plausibly expect an interpretation of the phenomenon to be found. Briefly, the suggested explanation is the following. Almost all discussions of the metallic state have used the Bloch theory, or some refinement of it like that developed by Wigner and Seitz. The essence of such a theory is the use of a model where each electron moves in a periodic potential field, and where a wave function for the whole crystal can be made up by assigning to each electron of the metal a different wave function in such a periodic field. Brillouin[2] has attempted to show that a wave function of this type can exhibit superconductivity, but the criticisms of his attempt are generally believed to show that this is impossible. Instead, it is generally thought that a correct theory must depend on some sort of cooperative action between the electrons, of a type not describable by Bloch's theory. Theories of this sort have been suggested by Kronig[3] and Frenkel;[4] but neither one has made close enough connections with the accepted theory of metals to lead to any real hope of solving the problem. In contrast to those attempts, we shall proceed by well-known methods, asking how we should expect Bloch's method to be in error, and how to correct this error. In atomic structure, the analog to Bloch's method is the one-electron method, treating each electron as if it moved in a central field, and building up a wave function by assigning to each electron an orbit in the central field. It is at once observed, however, that there is degeneracy; using these unperturbed wave functions, a number of states, corresponding to different orientations of orbits and spins, prove to have the same energy. We proceed by computing the nondiagonal components of the energy matrix between such states, and carrying out a perturbation calculation, which yields perturbed energy levels falling into the well-known multiplet classification, with perturbed wave functions which are linear combinations of a number of the unperturbed functions. In the problem of metals, the present suggestion is that we must take the Bloch theory only as a first approximation; that, on account of degeneracy, we must find nondiagonal energy components between Bloch states, and make linear combinations according to perturbation theory.

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[1] For a general review of superconductivity, with references, see H. G. Smith and J. O. Wilhelm, Rev. Mod. Phys. **7**, 237 (1935).

[2] L. Brillouin, J. de phys. et rad. **4**, 334 (1933); **4**, 677 (1933).

[3] R. de L. Kronig, Zeits. f. Physik **78**, 744 (1932); **80**, 203 (1933).

[4] J. Frenkel, Phys. Rev. **43**, 907 (1933).

Plausible reasons are given for the belief that, when this is done, while most of the energy levels of the electrons will not greatly change their nature, the very lowest states of the electronic system as a whole will be rather profoundly affected, and these will lead to the superconducting state. In the first section we consider this perturbation problem; in the second, we show that the resulting energy levels and wave functions may reasonably be connected with the existence of superconductivity.

1. Perturbations of Bloch Wave Functions

It is well known that the stationary states of an electron in a periodic potential field can be classified into certain energy bands. Each band contains a large number of levels, each of which can be occupied by one electron of each spin; in simple cases, a band contains as many levels as there are atoms in the crystal. The lowest stationary state of the crystal, on the Bloch picture, then arises when the electrons are placed in the lowest available levels. If the crystal is an insulator, the electrons will just fill some bands, leaving all the others entirely empty. For a metal, on the other hand, the number of electrons is such that one band at least is only partly full. If two or more bands overlap in energy at the top of the filled levels, each one will contain some electrons in its lower levels, but its upper levels will be unfilled. It is this case which we shall consider; for our considerations would indicate that the existence of more than one partly filled band is essential to superconductivity. For many purposes it is convenient to classify the levels according to the vector $\mathbf{k}$, the momentum or wave number vector, defined by the condition that the wave function is multiplied by a factor $\exp(i\mathbf{k}\cdot\mathbf{R})$ in going from one point of the lattice to a point removed by a distance $\mathbf{R}$, where $\mathbf{R}$ is the vector from the nucleus of one atom to that of another. We can then set up a $\mathbf{k}$ space, and can show that all the essentially different wave functions can be described by $\mathbf{k}$'s lying in a polyhedral cell surrounding the origin. Each energy band is represented by a set of $\mathbf{k}$ values filling this zone with uniform density. Energy contours can be drawn within the zone, and for the type of metal we are considering, there will be at least two zones for which only the levels within a certain energy contour will be filled.

Excited levels in the Bloch theory occur when one or more electrons are displaced from their original positions to other, necessarily higher, states. To a first approximation, the change in the energy of the system as a whole when an electron is displaced is given by the change in one-electron energy of this electron, and if only a few electrons are excited, we can add their separate excitation energies. It is now clear that above the lowest energy level of the system as a whole we have a continuum of excited levels. Any electron can be displaced to any unoccupied level; and if we choose to displace an electron which is just at the top of the occupied levels, and displace it to the bottom of the unoccupied ones, we shall do a negligible amount of work. There are so many electrons of this maximum energy, and so many unoccupied levels close above, that there are a great many states with energy hardly higher than the normal state. If the Bloch wave functions are correct, these excited levels of the system as a whole will really represent the excited levels of the metal. This will be the case if the matrix component of energy vanishes between any two levels of the continuum. But if these matrix components do not vanish, but instead have appreciable values, we must carry out a perturbation calculation; and since the states form a continuum, which is even worse than ordinary degeneracy, the perturbations may make important changes in the final energy levels and wave functions.

In the appendix, we consider the nondiagonal matrix component of energy between two Bloch states. We come to the following conclusions:

The matrix component is practically zero unless two, and only two, electrons have changed their levels from one state to the other.

The matrix component is zero unless the sum of the $\mathbf{k}$ vectors of all electrons is the same in the initial and final state. Since only two electrons are changing their $\mathbf{k}$'s, this means that the change in $\mathbf{k}$ of one should be equal and opposite to that for the other.

The matrix component is very small unless the two electrons which move in the transition were originally in two different energy bands;

and unless they are finally in two different energy bands. This shows that if we assume only one band to be partly occupied, as in an alkali metal, or Cu, Ag, Au, the Bloch states themselves will form good approximations, and no further perturbation calculation is necessary. Thus our theory would not lead to superconductivity for these metals, and it is significant that none of them have been observed to be superconducting.

In accordance with the matrix components just described, we can examine the perturbation problem. Let us start with a given low energy state of the metal as a whole, given by the Bloch theory. This will have matrix components to a great many other states, but we know from perturbation theory that the other states of almost the same energy will have the most effect. We shall therefore classify all the transitions from this state to others of about the same energy. In particular, we consider all transitions in which one electron changes its **k** value by $\Delta\mathbf{k}$, the other by $-\Delta\mathbf{k}$. We have two partly occupied energy bands, which we may call 1 and 2. Then we assume in the transition that an electron in band 1 goes into band 2, with change of $\Delta\mathbf{k}$, and an electron in band 2 goes into 1, with change of $-\Delta\mathbf{k}$. Furthermore, to have no appreciable increase of energy, each electron must have been originally at the top of the filled levels, and must have gone to the top of the filled levels in the other band. We may therefore obtain all the transitions of this type by the following construction. We start with our polyhedral zone, and plot in it the energy surface representing the top of the filled levels of band 1; we call this surface 1. Similarly we plot in the same zone the surface for band 2. We then displace surface 1 by the vector $\Delta\mathbf{k}$, and consider the line of intersection of the displaced surface 1 with surface 2. As a rule, these surfaces will actually intersect. Going back to the original surface 1, we can draw on it the line which was carried into the line of intersection by the displacement. Then we have lines on both surface 1 and surface 2, of the same shape, and the second displaced the amount $\Delta\mathbf{k}$ from the former. In other words, the electron which is removed in the transition from band 1 may come from any point of this line on surface 1, and by the displacement it will be carried to a point of the line on surface 2; and the electron which is removed in the transition from band 2 may come from any point of the line on surface 2, and by the equal and opposite displacement will be carried to a point on surface 1. If we allow a certain small tolerance in the energy values, it is clear that the surfaces will be replaced by thin shells, and their intersection by a thin filament of finite volume, so that there will be a finite number of such transitions for each value of $\Delta\mathbf{k}$, and a great many when we consider all possible values of $\Delta\mathbf{k}$. Thus it is clear that a given state will have nondiagonal matrix components to a great many other states, which however resemble it in having the same total number of electrons in each of the two bands, and in having the same vector sum of the **k**'s. Of course, if we allow transitions to states with appreciably different energies, we have a great many more.

We shall make no attempt to solve the extremely complicated perturbation problem presented in this way. We can, however, make certain statements regarding the nature of the solution. First, we consider the perturbed energy levels. The second order perturbation theory cannot be applied quantitatively in the perturbation of a continuum of levels, but it leads qualitatively to the correct result: each unperturbed level is, so to speak, pushed away from every other level with which it has a matrix component, by an amount proportional to the square of the matrix component, and inversely proportional to the energy difference between the unperturbed levels. This means that in the middle of a continuum, a level will be pushed approximately equal amounts in both directions, and will as a result hardly be affected by the perturbations. But at the edge of a continuum, the push is entirely one-sided, and will result in the few levels near the edge being shoved away from the others, so that they will spread out into energy regions previously unoccupied. In our case, the unperturbed continuum has a lower boundary, coming at the lowest energy of the metal as computed by the Bloch theory. The effect of perturbations will be to spread out the few lowest states, so that they will lie lower than they otherwise would, and will correspondingly have a lower density of states per unit energy range. Effectively, there will be a relatively small number of special states below the lowest Bloch states.

Next, we consider the wave functions. In such a perturbation of a continuum, the energy levels which are not much affected, lying in the middle of the continuum, will have wave functions which also are not much changed by the perturbation. But those which are repelled from the other states, at the bottom of the continuum, will have wave functions which are combinations of those unperturbed wave functions which do the repelling. Thus in our case one of these special states will have a wave function which is made up of all those Bloch states having the same vector sum of **k**'s, the same number of electrons in each of the two bands, and approximately the same energy; and we have seen that there are a great many such states. These states will all be on a par in the calculation, and will have approximately the same coefficients in the linear combination; states satisfying all the conditions except that they have appreciably different energy will also appear, but with smaller coefficients.

A simple example of such a perturbation problem has been worked out by the writer and Shockley,[5] in a discussion of the absorption of light by an alkali halide crystal. The problem there discussed was essentially the following, if considered from the present point of view: there are electrons in two bands, but in particular one band contains only one electron, the other has all its levels but one occupied. All such states consistent with a given vector sum of the **k**'s were set up, and the perturbation problem was solved, taking account of all these states. The problem was carried out only in one dimension, but this should hardly change the general results. It was carried out in terms of atomic functions rather than Bloch functions, but it is an easy matter to transform the unperturbed functions to the Bloch form. Thus it is seen that essentially this problem was specialized only in the small number of electrons in the second band, and while that simplifies the calculations greatly, it would hardly be expected to change the results profoundly. It was found, just as we have described in the preceding paragraph, that the energy levels and wave functions in the middle of the continuum were hardly affected by the perturbation, but that in this case just one level at the bottom split off, having an appreciably different energy, and a very different type of wave function, from the states of the continuum. Its wave function, as we have stated, was a combination of all the unperturbed functions, in which those of approximately the same energy are represented to approximately the same extent, but those of higher energy are not so strongly represented. While these results are not all at once apparent from the paper quoted, they can be derived from the discussion given there without difficulty.

The example mentioned above resembles the present problem not only mathematically, but fundamentally. To see this, let us adopt the same method used there, that of considering the energy levels of the system as a whole as a function of lattice spacing. To fix our attention on a definite case, let us consider the crystal of magnesium, which satisfies our condition of having two energy bands partly occupied, and which is known to be superconducting. At large distances, the band of $3s$ electrons is filled, the bands of $3p$ are entirely empty, so that the lowest state of the crystal is a single state, and the crystal would be an insulator. As with an alkali halide, the lowest excited state would come by removing one electron to the $3p$ band. If the bands are spread out at all, this will result in a continuum of excited states, depending on which $3s$ electron is removed, which $3p$ state it enters. But it was shown in the paper mentioned above that the very lowest excited states will not belong to the continuum. Instead, the lowest of all will come from the process which is described in an atomic model as excitation of the $3s$ electron of one atom to the $3p$ level of the same atom; next there will come discrete states arising from ionization of one atom, removing its $3s$ electron to the next nearest neighbor, and there creating a negative ion, with two $3s$ and one $3p$ electron; still further discrete levels will come from removal of the electron to further and further neighbors; and finally the continuum will arise from the process of removal of an electron from one atom to a distant atom, creating a widely separated pair of ions. These discrete levels lying below the continuum are

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[5] J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

most marked at large distances, but while more and more of them merge with the bottom of the continuum as the lattice spacing diminishes, some of them are still separated from the continuum at the actual lattice space.

Now let us see how the situation is affected by the fact that in magnesium at small distances the *3s* and *3p* energy bands broaden so that the higher energies in the *3s* band lie above the lower ones of the *3p* band. Let us consider the state where the *3s* band is full, the *3p* empty, as a zero of energy at all lattice spacings. Then at the point where the overlapping of bands commences, the bottom edge of the continuum of excited levels will have descended to touch this zero of energy, and at smaller lattice spacings it will be lower than the zero. In other words, the state where *3s* is full, *3p* is empty, is no longer the lowest state in the Bloch theory; the energy will be diminished if the highest *3s* electron goes into the lowest *3p* state. But all this time, there is a discrete state even below the bottom of the continuum of excited levels. Therefore at the actual distance of separation, if we had the artificial state where all *3s* levels were full, the transition of one electron which would make the greatest reduction in the energy of the system would not be a transition to an ordinary Bloch state at all, but rather would be this special type of transition, essentially to a state where the excited *3p* electron is attached to the same atom from which, as a *3s* electron, it was removed. Now this represents merely the gain in energy that can be produced by the transition of one electron; but clearly other electrons also will make transitions with reduction of energy, also to special states, until finally there will be an equilibrium.

We see, in other words, that by this method of tracing energy levels from large distances to small ones, just as by the direct perturbation method, we conclude that there will be special stationary states of the electrons of the system as a whole, lying slightly below the ordinary Bloch states, and representing special linear combinations of these low lying Bloch states, including a great many Bloch states with the same vector sum of the **k**'s, the same number of electrons in each of the partly occupied energy bands, and about the same energy. It would be very difficult to make any accurate calculation of the exact nature of these states, but we shall show in the next section that the simple properties already mentioned are enough to make it very plausible that these states should represent the superconducting state of the metal.

2. The Superconducting State

At any temperature, the probability of finding the whole system in a state of energy E will be proportional to $\exp(-E/kT)$. Thus at the absolute zero only the lowest of our special states will have any chance of being realized. At very low temperatures, since the special states lie below the Bloch states, the chances will be very good that the system will be found in a special state. But as the temperature rises, so that the exponential $\exp(-E/kT)$ is not too small for the Bloch states, the latter can be occupied. Now the number of Bloch states per unit energy range will be enormously greater than the corresponding number for the special states. Thus when the probability that the Bloch states can be occupied at all becomes appreciable, on account of their great number the chance will become practically a certainty that the system will be found in the Bloch states. There will be, then, a gradual, but in the end an extremely rapid, change from the special to the Bloch type of state, as the temperature is increased. As we shall see, this is what is observed.

To an approximation, we may take the special states as representing one phase of the electrons, the Bloch states as another, forgetting that one sort really will merge smoothly into the other. The special phase will have a lower internal energy at the absolute zero of temperature than the Bloch phase; that is, the lowest special state has a lower energy than the lowest Bloch state. But, in thermodynamic language, the entropy of the special state at any temperature will be negligible compared with the entropy of the Bloch phase. The reason for this is that the entropy of a phase depends essentially on the number of stationary states which belong to that phase. Then we can get the equilibrium condition of the phases thermodynamically by equating the thermodynamic potentials Z of the two phases. At zero pressure, the thermodynamic potential may be written $Z=E_0-\int_0^T SdT$, where E_0 is the internal energy at the absolute zero, S is the entropy as a function of the temperature T. Thus we see that the thermodynamic potential of the special phase will be approximately independent of temperature. On the other hand, for the Bloch state, the specific heat C_p is known to be proportional to the temperature, equal say to $C_p=AT$. Then the entropy is given by $S=\int C_p/TdT=AT$, so that the thermodynamic potential is $E_0-AT^2/2$. In other words, while the Bloch state has a higher thermodynamic potential than the special state at the absolute zero, its potential decreases with temperature. If ΔE represents the energy difference between the special and Bloch states at the absolute zero, it is clear that our approximation shows that the potentials of the two states should become equal when $\Delta E=AT^2/2$, $T=(2\Delta E/A)^{\frac{1}{2}}$, and that above this temperature the ordinary Bloch state should be the stable one. From known temperatures of transition and values of A we can get an approximate idea of the order of magnitude of ΔE necessary to explain superconductivity. Thus for silver A is of the order of magnitude of 0.00015 calorie per mole per degree. (We choose a nonsuperconducting metal to determine the value of A, since the superconducting ones cannot be followed to low enough temperatures in the Bloch state to separate the linear part of the specific heat from the T^3 part arising from the Debye function.) For most superconducting elements, the transition temperature is a few degrees absolute. Take for instance 7 degrees for T. Then ΔE becomes 0.0038 calorie per mole $=1.6\times10^{-7}$ electron volts per atom. In other words, our special states need be depressed below the Bloch continuum by only an excessively small energy of this order of magnitude to explain superconductivity.

The calculation we have just made seems to show without further hypothesis why the elements of the transition group (W, Fe, Ni, Pt in particular) have not been found to be superconducting. It is known that these elements have abnormally large values of the electronic specific heat, on account of their unfilled inner shells; that is, they have abnormally large values of the constant A, sometimes as large as 30 or 40 times the normal size. Then, if they have values of ΔE comparable with other metals, our formula shows that the transition temperature should be something like $\sqrt{40}$ times smaller, or six times smaller, than normal values. In other words, it seems plausible that these elements may really be superconducting, but that low enough temperatures have not yet been reached to show the effect. It is notable that our two categories of elements, first the alkalies and Cu, Ag and Au, and second the transition elements, include almost all the elements which have definitely been observed not to be superconducting at temperatures so far obtained.

The approximation of representing the superconducting and ordinary states of a metal as two phases, which we have just considered, is known to be a fair approximation, as is shown by the work of Rutgers, Gorter, Casimir, and others.[6] These writers have made a thorough study of the thermodynamics of superconductivity, and have shown, just as we have indicated, that the superconducting state must really have practically no entropy. They have further shown that if the superconducting state shields a conductor magnetically, as a perfect conductor should, the magnetic induction B will automatically be zero inside the conductor, and this introduces a magnetic term into the thermodynamic potential which automatically produces a change of equilibrium temperature with magnetic field, in quantitative as well as qualitative agreement with experiment. Thus we do not need to discuss the magnetic effect on the equilibrium between states. Furthermore, they have shown that the approximation of an ordinary phase change is too crude. In the absence of a magnetic field, there is no latent heat at the transition point, only a discontinuity of the specific heat, which means thermodynamically that the first derivative of Z with respect to T is not discontinuous, but only the second derivative. This suggests that the superconducting state really merges gradually into the ordinary state as the temperature rises. But that is just what our model would lead us to suspect; for there is no perfectly sudden change between our special states and the Bloch states, only a gradual change, which

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[6] A. J. Rutgers, Physica **1**, 1055 (1934); C. J. Gorter and H. Casimir, Zeits. f. tech. Physik **15**, 539 (1934); J. A. Kok, Physica **1**, 1103 (1934); etc.

cannot be correctly described by dividing the states sharply into two classes. Thus we may conclude that as far as thermodynamic properties are concerned, our model of the superconducting state certainly shows the right general behavior, and does not contradict the known and well worked out theory in any particular.

In addition to the fact that the superconducting state forms a special phase of the electrons at low temperatures, which probably is the most fundamental property of this state, there remains its remarkable property of being able to carry a current for an indefinite time, without its dissipation in Joulean heat. This means that the probability of scattering of the electrons by the thermal motion of the lattice is zero, or excessively small, in the superconducting state. Now it is well known that the study of this scattering, and the deduction of the value of the resistance, is extraordinarily difficult for very low temperatures even in a normal metal; and we shall make no attempt to investigate the resistance of our special electronic states, and to show that the resistance is zero. There is, however, one fact which makes it very plausible that the resistance should vanish. The ordinary formula for resistance based on the Bloch theory contains as a factor the square of the density of one-electron energy levels at the top of the occupied levels. The reason for this is that the larger the number of unoccupied levels available for an electron to be scattered into, the larger is the probability of its being scattered. This idea has been used by Mott[7] to explain the large resistance of the transition metals, in terms of the large number of unoccupied states in the partly filled bands of d electrons. The argument is ordinarily stated in terms of one-electron levels; but it is clear that what is needed for large resistance is a large number of energy levels of the metal as a whole per unit energy range, in the neighborhood of its lowest level. It is significant that the same metals which, according to Mott, have an abnormally high resistance, are those which also have an abnormally high electronic specific heat, and therefore an abnormally high electronic entropy; for both these things come from the excess of energy levels.

Now the situation in our model of the superconducting state is just the opposite. In the neighborhood of the lowest energy level of the metal, the levels are spread out by the perturbation so that an extremely small number of levels comparatively is spread through a finite interval of energy. In other words, the number of available energy levels per unit range of energy, which an electron can be scattered into, is much smaller than normal. It is so much smaller that as we have seen the entropy appears to be practically equal to zero. By the same argument as before, then, the probability of electron scattering should be very much less for these states than for the normal states, and the resistance should be very much smaller. If this argument, which it is admitted is only qualitative, should be correct, the lack of resistance of the superconducting state would be tied up with its lack of entropy, and any theory which would explain one would explain the other. It would be very desirable to check this suggestion by an actual calculation of the distribution of the superconducting energy levels, and of the corresponding conductivity of the metal. But in the present state of the electron theory, this would be almost prohibitively difficult. Under the circumstances, it seems worth while bringing forward this tentative model of the superconducting state, even though it is only qualitative. If this state can be explained in terms of existing theories at all, it seems almost inevitable that it will be in some such way as is suggested here, in terms of further approximations starting with the Bloch theory as a beginning. And it seems significant that one can give at least likely reasons why such an attempt might be successful.

APPENDIX

The one-electron functions which we shall assume will be real solutions of the periodic potential problem, rather than Bloch's approximations to these solutions by means of atomic functions. Then the functions will be orthogonal to each other, and when we build up a function for the whole crystal, in the form of a determinant, the relations as far as matrix components of the energy are concerned will be as in the atomic problem. As in that problem, the non-diagonal matrix components of energy will come from the terms $2/r_{ij}$ in the potential energy, and will arise between

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[7] N. F. Mott, Proc. Roy. Soc. **A153**, 699 (1936); *The Theory of the Properties of Metals and Alloys* (Oxford, 1936).

states differing in the wave functions of two electrons at most. If the initial wave functions of these two electrons are symbolized by A, B and the final ones by C, D, then it can be shown that the matrix component will be just as for a two-electron problem involving only these two electrons:

$$\tfrac{1}{2}\int\begin{vmatrix} A^*(1) & B^*(1) \\ A^*(2) & B^*(2)\end{vmatrix}(2/r_{12})\begin{vmatrix} C(1) & D(1) \\ C(2) & D(2)\end{vmatrix}dv_1dv_2.$$

If now A, B, C, D represent modulated functions, it is easy to show that unless the sum of the $\mathbf{k}$'s for A and B equals the sum for C and D, the integral over the crystal will vanish. If this condition is satisfied, however, the integration of dv_1 only over the cell surrounding one atom will lead to just $1/N$th of the whole integral, if N is the number of atoms. Furthermore, if dv_1 is integrated over one cell, the major contribution to the integral will come when dv_2 is integrated over the same cell. Now within a given cell, the wave functions of all the states of a single band are similar. Thus if A and B refer to states of the same band, the first determinant will be small, and if C and D states of the same band the second determinant will be small, verifying our statement that the matrix component is large only when A and B refer to different bands, and C and D refer to different bands.

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Approximation to Discrete Quantum States by Iteration

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A method is described by which successive approximations to the wave functions and energies of stationary states can sometimes be obtained in a form allowing definite limits of error to be stated. Two examples in which the solution is otherwise known are worked out and the rate of approximation is found to be rapid.

The Iteration Process

CONSIDER the homogeneous linear equation

$$N\psi=\lambda D\psi, \qquad (1)$$

where N and D are two Hermitian operators operating on a range of functions ψ of certain variables x. Suppose a function φ_0 in the range can be expanded in the series

$$\varphi_0=c_1\psi_1+c_2\psi_2+\cdots, \qquad (2)$$

where ψ_r are proper functions of (1) corresponding to proper values λ_r (some of which may be distributed continuously). Then, if we operate on φ_0 repeatedly with $N^{-1}D$ giving the sequence of functions φ_1, φ_2, $\cdots$ such that

$$N\varphi_{n+1}=D\varphi_n, \qquad (3)$$

we shall have $\varphi_n=\lambda_1^{-n}c_1\psi_1+\lambda_2^{-n}c_2\psi_2+\cdots$. (4)

Thus, if Eq. (1) has a discrete proper value of lowest absolute value, λ_s, and if the coefficient of the corresponding proper function ψ_s in φ_0, *viz.* c_s, does not vanish,

$$\varphi_n\sim\lambda_s^{-n}c_s\psi_s \quad (n\rightarrow\infty), \qquad (5)$$

converging geometrically: and we have a process for approximating to ψ_s.

When a function φ approximating ψ_s has been found, if Eq. (1) has a discrete proper value next lowest in absolute value to λ_s, we can approximate in like manner to its corresponding proper function by replacing φ_n at each stage by

$$\varphi_n-\{(\psi^*\varphi_n)/(\psi^*\psi)\}\psi, \qquad (6)$$

where ψ^* is the (Hermitian) conjugate to ψ and $(\psi^*\psi)$ means their summed product.

Limits of Error

We can usually find from an approximate proper function ψ, by modifying it if necessary so that the zeros of $N\psi'$ and $D\psi'$ coincide, a function ψ' such that bounds μ and ν exist for which

$$\mu\leq(N\psi'/D\psi')\leq\nu \quad \text{(all } x). \qquad (7)$$

There is then a corresponding proper value λ of (1) satisfying

$$\mu\leq\lambda\leq\nu. \qquad (8)$$

If in particular D is positive definite, and if Eq. (1) has a discrete lowest proper value, λ_1,