AUGUST 1, 1937 PHYSICAL REVIEW VOLUME 52

The Theory of Ferromagnetism: Lowest Energy Levels

J. C. SLATER
*Institute for Advanced Study, Princeton, New Jersey**

(Received May 7, 1937)

The theory of ferromagnetism is formulated both by the method of energy bands and the method of spin waves, and the connection between them is investigated. The particular problem considered is that where N-1 electrons in a band have one spin, one electron the opposite spin. Each method yields a set of unperturbed wave functions, each of which can be expressed in terms of the other. Neither represents the true situation, which must be found by perturbation theory. The final result is that below the continuum of levels indicated by the energy band theory there is a set of discrete levels. The lowest of these is essentially a spin wave, and is the state ordinarily occupied. For investigating the temperature variation of magnetization, the spin wave theory should be used. On the other hand, the energy band theory leads to approximately correct conclusions as to which elements should be ferromagnetic. The formulation is in terms of orthogonal atomic functions, which have advantages compared with the nonorthogonal functions usually employed. In the limit of broad energy bands, and nonferromagnetic substances, the discrete levels approach the continuum, and their wave functions represent a situation in which the electron of negative spin can wander to a considerable distance from the positive ion which it has left, but not to infinite distance.

THE theory of ferromagnetism has been treated by several distinct methods. In the first place, Heisenberg's[1] original theory was based on the Heitler and London method in molecular structure, each electron being localized on a particular atom, and Bloch's[2] theory of spin waves, and Bethe's[3] extension of that theory, were based on Heisenberg's work. On the other hand, Bloch[4] worked out a theory of the ferromagnetism of free electrons, based on the theory of energy bands. This type of theory has been adapted by the present writer[5] to a discussion of the ferromagnetism of nickel. Both methods have advantages and disadvantages. Heisenberg's type of theory has in the first place the great advantage that it makes direct connection with the familiar Weiss theory of ferromagnetism, though it does not agree with that theory in all details. Furthermore, it reduces to the proper limiting values when the atoms of the crystal are removed to infinite separation from each other. It has, however, three great disadvantages. The first is that it does not change over continuously to a theory of metallic conduction electrons, when proper changes are made in the various parameters involved. It is known that this is a result of the failure to include polar states in the formulation, states where atoms can carry a net charge. The second disadvantage is that it does not lead in any very clear way to an understanding of why some elements are ferromagnetic, others not. The exchange integral which determines ferromagnetism must be of opposite sign to its normal value for ferromagnetism to occur, and while plausible reasons have been given to suppose that it actually has this sign in the ferromagnetic elements, these reasons have not, as far as the writer knows, been strengthened by an actual calculation of the exchange integral. The third disadvantage is a rather technical, but none the less a very important, one: the wave functions with which one operates are not orthogonal, with the result that there are many exchange integrals between three and more electrons, which are generally neglected in the simple form of the theory, but which are actually not negligible. Van Vleck[6] has recently shown how to handle this lack of orthogonality, but even if it can be taken care of, it seriously complicates the calculations.

The theory based on energy bands likewise has its advantages and disadvantages. Greatest of the advantages is probably the fact that it makes direct connection with the theory of conductivity, of cohesion, and of other metallic properties, all now handled most satisfactorily

---

* On leave from the Massachusetts Institute of Technology, Cambridge, Mass.

[1] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

[2] F. Bloch, Zeits. f. Physik **61**, 206 (1930).

[3] H. Bethe, Zeits. f. Physik **71**, 205 (1931).

[4] F. Bloch, Zeits. f. Physik **57**, 545 (1929).

[5] J. C. Slater, Phys. Rev. **49**, 537, 931 (1936).

[6] J. H. Van Vleck, Phys. Rev. **49**, 232 (1936).

by energy bands. Secondly, it leads to a clear understanding, based on approximate calculations, of the reason why ferromagnetism occurs where it does in the periodic table. Thirdly, it is based throughout on orthogonal functions, greatly simplifying the calculations. Finally, the theory of energy bands has reached a stage where fairly satisfactory numerical calculations can be made, so that it is not hard to make our information fairly quantitative. On the other hand, this theory also has serious disadvantages. It leads to quite wrong values in the limiting case of large separation of the atoms, and this is likely to be particularly serious, since the energy bands responsible for ferromagnetism are narrow, corresponding to atomic orbits which are widely separated in proportion to their size. Furthermore, it makes no connection with Weiss's theory, and with the valuable way of visualizing the problem which that theory provides. We must conclude that neither method by itself is very satisfactory.

This is no newly appreciated situation. The writer in 1930[7] called attention to it, and pointed out that energy band functions on the one hand, or atomic functions of Heisenberg's type, augmented by polar states, on the other, formed two possible starting points for a perturbation calculation. Either set of functions can be written as linear combinations of the functions of the other set. A correct linear combination of the functions of either set will then yield a more satisfactory approximation than functions of either set separately. In other words, we can make a theory more satisfactory than either Heisenberg's or the energy band theory, and the final result will be independent of which we use as a starting point. These remarks were illustrated at the time by the hydrogen molecule H_2, which can be treated by analogous theories, but it was not possible then to make detailed calculations for the problem of ferromagnetism, which was not the primary concern of the paper mentioned. Since then, Schubin and Wonsowsky[8] have extended the use of polar states, obtaining results analogous to some of those in the present paper. The writer and Shockley[9] recently discussed the very similar problem of absorption of light by the alkali halides, and the method there used can be adapted to ferromagnetism. Furthermore, recent work of Wannier[10] has provided us with orthogonal atomic functions, which simplify the problem greatly. It therefore seems worth while to approach the general theory again, with a view to finding the best solution of the problem intermediate between the Heisenberg and the energy band type of theory. The present paper contains a first step in this direction. We consider only a single energy band, which in its lowest state contains just one electron per atom of one spin, none of the other spin. And we consider just the case where one electron only is disturbed from this state, reversing its spin, raising the energy of the system if it is ferromagnetic, or lowering it if it is not. This is essentially the same problem considered in Bloch's theory of spin waves,[2] but supplemented by polar states, allowing the connection with the theory of energy bands to be made. Though this case is much simpler than the real situation, still it is instructive. The result is a theory which reduces precisely in one limit to the theory of energy bands, and in another limit to something very much like the Heisenberg theory, possessing all the advantages of that theory, but the additional great advantage of dealing only with orthogonal functions. The intermediate case, representing the actual state of affairs, proves to resemble the theory of energy bands in the criterion for ferromagnetism, verifying in a general way the results of the author's calculation[5] that the elements of the iron group should be ferromagnetic. But the actual lowest states of the system are described by something much more like Bloch's spin waves, so that Bloch's calculation of the temperature variation of saturation magnetization at low temperatures should be correct. The present paper, like Bloch's, is limited to low temperatures, since we can only treat the case where one electron has its spin reversed, or practically the case where there are so few reversed spins that they rarely interact with each other.

---

[7] J. C. Slater, Phys. Rev. **35**, 509 (1930).

[8] S. Schubin and S. Wonsowsky, Proc. Roy. Soc. **A145**, 159 (1934).

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

[10] G. Wannier, Phys. Rev. (preceding paper, this issue).

THE UNPERTURBED WAVE FUNCTIONS

We shall start with the method of energy bands. Imagine a periodic potential $U(\mathbf{r})$, where $\mathbf{r}$ is a vector coordinate. We shall later determine $U(\mathbf{r})$ by a Fock-Hartree self-consistent field method. We shall now imagine that we have the exact solutions for the motion of an electron in this potential. We consider only one energy band, containing N energy levels of each spin, where N is the number of atoms in the crystal (or in the repeating region of space, using periodic boundary conditions). Let the wave function associated with the wave vector $\mathbf{k}$ be $b(\mathbf{k}, \mathbf{r})$, so that it is multiplied by $\exp(i\mathbf{k}\cdot\mathbf{R})$ in traveling from one cell to another distant by the vector $\mathbf{R}$. Let the energy as a function of $\mathbf{k}$ be $W(\mathbf{k})$. Since we are dealing with only one band, we may always imagine $\mathbf{k}$ to be in the central cell of $\mathbf{k}$ space. Using atomic units, the functions then satisfy the Schrödinger equation

$$(-\nabla^2+U(\mathbf{r}))b(\mathbf{k}, \mathbf{r})=W(\mathbf{k})b(\mathbf{k}, \mathbf{r}). \qquad (1)$$

We shall often have occasion to use atomic functions, rather than the periodic functions $b(\mathbf{k}, \mathbf{r})$. For this purpose we shall use Wannier's orthogonal functions:[10]

$$a(\mathbf{r}-\mathbf{R})=1/(N)^{\frac{1}{2}}\sum_{\mathbf{k}} \exp\left[(-i\mathbf{k}\cdot\mathbf{R})\right]b(\mathbf{k}, \mathbf{r}). \qquad (2)$$

Here $\mathbf{R}$ is the radius vector to one of the nuclei, and the summation is over the N vectors $\mathbf{k}$ in the central cell. We can easily prove that the a's are orthogonal, and normalized if the b's are normalized:

$$\int a^*(\mathbf{r}-\mathbf{R})a(\mathbf{r}-\mathbf{R}')d\tau=(1/N)\sum_{\mathbf{k},\,\mathbf{k}'} \exp\left[i(\mathbf{k}\cdot\mathbf{R}-\mathbf{k}'\cdot\mathbf{R}')\right]\int b^*(\mathbf{k}, \mathbf{r})b(\mathbf{k}', \mathbf{r})d\tau$$
$$=(1/N)\sum_{\mathbf{k}} \exp\left[i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')\right], \qquad (3)$$

on account of the orthogonality and normalization of the b's. But it is a property of the reciprocal lattice that the expression on the right side of (3) is zero if $\mathbf{R}-\mathbf{R}'$ is a vector between two lattice points which is different from zero, but is unity if $\mathbf{R}-\mathbf{R}'$ is zero. Hence the orthogonality and normalization of the a's are proved. In the future we shall often use the property of summing over $\mathbf{k}$ which we have just mentioned, and also the other property that the same summation mentioned in (3), but now summed over all atoms $\mathbf{R}'$ rather than over all wave vectors $\mathbf{k}$, is zero unless $\mathbf{k}$ equals zero, in which case it is unity.

The summation in (2), by which the a's are expressed as functions of the b's, is such that $a(\mathbf{r}-\mathbf{R})$ is largely concentrated about the nucleus at $\mathbf{R}$, and resembles on that nucleus the atomic function of the isolated atom. The function changes sign on the nearest neighbors, however, so as to result in orthogonality, and in fact oscillates in sign, with rapidly decreasing amplitude, as we go away from the nucleus at $\mathbf{R}$. As the atoms become widely separated, if $U(\mathbf{r})$ approaches the potential of an isolated atom about each nucleus, $a(\mathbf{r}-\mathbf{R})$ approaches the corresponding atomic wave function of the isolated atom. The function $a(\mathbf{r}-\mathbf{R})$ is not conveniently written as the solution of an ordinary Schrödinger equation; we shall instead express its differential equation through the transformation (2), in terms of the Eq. (1) for the functions $b(\mathbf{k}, \mathbf{r})$.

We shall now set up unperturbed wave functions for the whole system, in terms of the functions $b(\mathbf{k}, \mathbf{r})$. First we consider the state where all N electrons have $+$ spins. Then the wave function is simply the determinant of functions b, using all values of $\mathbf{k}$ and the $\mathbf{r}$'s of all electrons:

$$B(0)=1/(N!)^{\frac{1}{2}}\left|b(\mathbf{k}, \mathbf{r}_i)\right|. \qquad (4)$$

This state $B(0)$ will be the lowest state in the ferromagnetic case. Next we consider the states where $(N-1)$ electrons have $+$ spin, one has $-$ spin. The process of setting up these states is almost exactly as in the paper on absorption by the alkali halides.[9] We consider in particular a state in which the electron with $+$ spin, and wave vector $\mathbf{k}-\mathbf{K}$, is missing, but in which there is an electron with $-$ spin, with wave vector $\mathbf{k}$. The corresponding wave function is defined as $B(\mathbf{k}-\mathbf{K}, \mathbf{k})$, and it differs from (4) in that the elements of the row equal to $b_+(\mathbf{k}-\mathbf{K}, \mathbf{r}_i)$ in (4) are missing, and are replaced by the elements $b_-(\mathbf{k}, \mathbf{r}_i)$. There are N^2 such states, corresponding to all N possible values of $\mathbf{k}$ and $\mathbf{K}$. It is easily shown, however, that the matrix components of energy, and of all periodic operators, are zero between states of different $\mathbf{K}$ value. This quantity $\mathbf{K}$ is at once seen to measure the total wave vector of all electrons in the excited state. Thus states with different $\mathbf{K}$ do not combine. Our perturbation problem will be one between the N states of a given $\mathbf{K}$. We shall have to find matrix components of the energy between them, and find the suitable linear combinations to give the correct solutions of the problem.

In addition to these functions B, we shall use excitation functions $F(\mathbf{K}, \mathbf{R})$, similar to the functions E and F introduced in reference (9). We define

$$F(\mathbf{K}, \mathbf{R})=1/(N)^{\frac{1}{2}}\sum_{\mathbf{k}} \exp\,[i\mathbf{k}\cdot\mathbf{R}]B(\mathbf{k}-\mathbf{K}, \mathbf{k}). \quad (5)$$

By methods similar to those of reference 9, we can show that $F(\mathbf{K}, \mathbf{R})$ can be made up in the following way. Starting with the lowest wave function $B(0)$, we describe the system by atomic functions $a(\mathbf{r}-\mathbf{R}_i)$. Then we remove the electron of $+$ spin from the atom $\mathbf{R}_i$, reverse its spin, and place it on the atom at $\mathbf{R}_i+\mathbf{R}$, producing a positive ion if $\mathbf{R}\neq 0$, though there are no ions produced if $\mathbf{R}=0$. We now combine all such functions from different atoms $\mathbf{R}_i$, multiplying each by a factor $1/(N)^{\frac{1}{2}} \exp i\mathbf{K}\cdot\mathbf{R}_i$, and adding. The function $F(\mathbf{K}, 0)$ then corresponds to Bloch's spin wave, except that our atomic functions a do not agree exactly with the atomic functions of Heisenberg's theory, and the functions $F(\mathbf{K}, \mathbf{R})$ with $\mathbf{R}\neq 0$ are the polar states which must be included to supplement Heisenberg's theory.

MATRIX COMPONENTS OF ENERGY

We must next set up the matrix components of the energy of the whole system. This is most easily done first in the system of B functions, and later we can find the components in the F system by transformation theory. The first step is to define the potential field U. We assume each atom to consist of a nucleus, and enough electrons in closed shells to leave it a singly charged positive ion, so that the one remaining electron which we are considering in our perturbation problem will make it neutral. Let $V(\mathbf{r})$, where $\mathbf{r}$ is the vector position, represent the potential due to the nuclei and closed shells of all the atoms, averaged in a suitable manner. This will be a sum of terms, one from each atom, and each falling off inversely as the distance at a distance from the nucleus, but behaving differently within the closed shells. In order to get $U(\mathbf{r})$ from $V(\mathbf{r})$, we must add the potential of the electrons in the states we are considering. In the first place, if all functions $b(\mathbf{k}, \mathbf{r})$ were occupied with one electron each, the electronic charge density would be $\sum_{\mathbf{k}} b^*(\mathbf{k}, \mathbf{r})b(\mathbf{k}, \mathbf{r})$, so that we should have to add the potential

electron potential=

$$\int \sum_{\mathbf{k}} b^*(\mathbf{k}, \mathbf{r}_j)b(\mathbf{k}, \mathbf{r}_j)(2/|\mathbf{r}_{ij}|)d\tau_j. \quad (6)$$

This is the potential, at point $\mathbf{r}_i$, of the distributed charge in elements $d\tau_j$, at distance $\mathbf{r}_{ij}$ from $\mathbf{r}_i$. By means of Eq. (2) or its inverse, we can express the electron potential in terms of atomic functions. It is then

electron potential=

$$\int \sum_{s} a^*(\mathbf{r}_j-\mathbf{R}_s)a(\mathbf{r}_j-\mathbf{R}_s)(2/|\mathbf{r}_{ij}|)d\tau_j. \quad (7)$$

The potential (6) or (7) is not exactly the correct one to use, however, for it is the potential of N electrons acting on the electron we are interested in, whereas actually only $N-1$ electrons are left to act on it, and on account of exchange, or the Pauli principle, the one electron missing from the distribution is removed from the immediate neighborhood of $\mathbf{r}_i$, so that it has an important effect on the potential. Remembering the orthogonality of the b's and a's, and the fact that in the lowest state all electrons have the same spin, this exchange charge density, at the point $\mathbf{r}_j$, when the electron we are interested in as at $\mathbf{r}_i$, is given by[11]

---

[11] J. C. Slater, Rev. Mod. Phys. 6, 267 (1934).

$$\Big\{\sum_{\mathbf{k}}\sum_{\mathbf{k}'} b^*(\mathbf{k},\mathbf{r}_i)b(\mathbf{k}',\mathbf{r}_i)b^*(\mathbf{k}',\mathbf{r}_j)b(\mathbf{k},\mathbf{r}_j)\Big\}\Big/\Big\{\sum_{\mathbf{k}''} b^*(\mathbf{k}'',\mathbf{r}_i)b(\mathbf{k}'',\mathbf{r}_i)\Big\}$$
$$=\Big\{\sum_s\sum_t a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_t)a^*(\mathbf{r}_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_s)\Big\}\Big/\Big\{\sum_v a^*(\mathbf{r}_i-\mathbf{R}_v)a(\mathbf{r}_i-\mathbf{R}_v)\Big\}. \quad (8)$$

From the second of expressions (8) we can see particularly easily that the exchange charge density is located in the neighborhood of $\mathbf{r}_i$. If $\mathbf{r}_i$ is in the neighborhood of the nucleus at $\mathbf{R}_i$, then terms like $a(\mathbf{r}_i-\mathbf{R}_s)$ will be much larger for $s=i$ than for any other value of s. Hence in the summations over s, t, and v the leading term will be that for which $s=t=v=i$. Then expression (8) reduces simply to $a^*(\mathbf{r}_j-\mathbf{R}_i)a(\mathbf{r}_j-\mathbf{R}_i)$, the distribution about the nucleus $\mathbf{R}_i$. This approximation becomes exact as the atoms become separated from each other. Now from the exchange charge density (8) we can set up the exchange potential:

exchange potential =

$$\left\{\sum_s\sum_t a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_t)\int a^*(\mathbf{r}_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_s)(2/|\mathbf{r}_{ij}|)d\tau_j\right\}\Big/\left\{\sum_v a^*(\mathbf{r}_i-\mathbf{R}_v)a(\mathbf{r}_i-\mathbf{R}_v)\right\}. \quad (9)$$

In terms of these quantities, we then have

$$U(\mathbf{r}_i)=V(\mathbf{r}_i)+\text{electron potential} -\text{exchange potential}. \quad (10)$$

From what we have just seen, this potential U behaves as it should when the atoms become widely separated; that is, it reduces near each nucleus to the potential of that nucleus and the electrons surrounding it, unaffected by the other atoms. Since the electrons all have parallel spins, no correction for correlation is necessary in addition to the exchange correction. Although the potential we have set up is strictly correct only for the lowest state, we use it as well for the states we are particularly interested in, where all electrons but one are parallel, the remaining one antiparallel. This approximation will make a negligible error, and is entirely justified in the present case, though it might not be if we were considering states with many antiparallel spins.

Next we must find the matrix components of energy. The energy operator for the whole system is

$$H=-\sum_i\nabla_i^2+\sum_i V(\mathbf{r}_i)+\sum_{\text{pairs }ij}2/|\mathbf{r}_{ij}| +\sum_{\text{pairs }st}2/|\mathbf{R}_{st}|. \quad (11)$$

The first term is the kinetic energy, the second the potential energy of electrons in the field of the nuclei and inner shells, the third the repulsion of electrons, the fourth the repulsion of the positive ions. Aside from the last term, which does not depend on the electron coordinates at all, we have two types of term: the first and second, a sum of one-electron operators, and the third, a sum of two-electron operators. Remembering that the one-electron functions are orthogonal, the diagonal component of the energy matrix equals the sum of the one-electron matrices between all one-electron functions, plus the sum of two-electron matrices between all pairs of functions, minus the sum of two-electron exchange integrals between all pairs with parallel spins. For the lowest state, then, we have in a simple notation

$$(B(0)|H|B(0))=\sum_{\mathbf{k}}(b(\mathbf{k},\mathbf{r})|-\nabla^2+V|b(\mathbf{k},\mathbf{r}))$$
$$+\sum_{\text{pairs }s,\,t}\int\int a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_s)a^*(r_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_t)2/|\mathbf{r}_{ij}|d\tau_{ij}$$
$$-\sum_{\text{pairs }s,\,t}\int\int a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_t)a^*(\mathbf{r}_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_s)2/|\mathbf{r}_{ij}|d\tau_{ij}+\sum_{\text{pairs }s,\,t}2/|\mathbf{R}_{st}|, \quad (12)$$

where we have used the functions b for the one-electron operators, the a's for the two-electron ones, for reasons of convenience. We find the Laplacian operators from Eq. (1), substitute for $U(\mathbf{r})$ from Eq. (10), remember that a summation over all values of s and t independently equals twice the summation over all pairs, and finally change all terms over to dependence on the a's rather than the b's. Then we find

$$(B(0)|H|B(0))=E_0=\sum_{\mathbf{k}} W(\mathbf{k})+\sum_{\text{pairs } s,\, t} 2/|\mathbf{R}_{st}|$$

$$-\sum_{\text{pairs } s,\, t}\int\int a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_s)a^*(\mathbf{r}_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_t)2/|\mathbf{r}_{ij}|d\tau_{ij}$$

$$+\sum_{\text{pairs } s,\, t}\int\int a^*(\mathbf{r}_i-\mathbf{R}_s)a(\mathbf{r}_i-\mathbf{R}_t)a^*(\mathbf{r}_j-\mathbf{R}_t)a(\mathbf{r}_j-\mathbf{R}_s)2/|\mathbf{r}_{ij}|d\tau_{ij}. \quad (13)$$

We shall use this energy E_0 simply to establish a zero of energy. If, however, we were interested in cohesion, its variation with lattice spacing would give us the total energy of the crystal. Since there is only one valence electron per atom, the terms other than the first will approximately cancel,[12] leaving the sum of $W(\mathbf{k})$'s as the approximate energy. (Of course, our model is really very deficient for a ferromagnetic substance. The electrons we are considering correspond to the $3d$ electrons in the ferromagnetic elements, and we neglect entirely the valence electrons which produce the binding.) In the limit of large internuclear distances, this relation becomes exact, and since the $W(\mathbf{k})$'s all coincide, and equal the atomic energy, at large distance, this leads to the correct energy for the lowest state of the system.

Next we find the diagonal energy $(B(\mathbf{k}-\mathbf{K},\mathbf{k})|H|B(\mathbf{k}-\mathbf{K},\mathbf{k}))$ for one of our states with a reversed spin. Most of the terms will be the same as those already considered in (12) or (13), and we shall simply consider the terms which are different. As far as the one-electron operators are concerned, we must eliminate the terms coming from $b(\mathbf{k}-\mathbf{K},\mathbf{r})$, and add extra terms coming from $b(\mathbf{k},\mathbf{r})$. It is more convenient in these expressions to retain the functions b, rather than writing in terms of atomic functions, since $\mathbf{k}$ appears explicitly in the final result. Then we find without complications that the one-electron operators give terms differing from those of (12) by

$$W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})+\sum_{\mathbf{k}'}\int(b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}-\mathbf{K},\mathbf{r}_1)-b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1))b^*(\mathbf{k}',r_2)b(\mathbf{k}',\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}$$

$$-\sum_{\mathbf{k}',\,\mathbf{k}''}\sum\int\{(b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}-\mathbf{K},\mathbf{r}_1)-b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1))b^*(\mathbf{k}',\mathbf{r}_1)b(\mathbf{k}'',\mathbf{r}_1)$$

$$\times b^*(\mathbf{k}'',\mathbf{r}_2)b(\mathbf{k}',\mathbf{r}_2)\}/\{\sum_{\mathbf{k}'''}b^*(\mathbf{k}''',\mathbf{r}_1)b(\mathbf{k}''',\mathbf{r}_1)\}2/|\mathbf{r}_{12}|d\tau_{12}. \quad (14)$$

The two-electron operators give terms differing by

$$-\sum_{\mathbf{k}'}\int(b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}-\mathbf{K},\mathbf{r}_1)-b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1))b^*(\mathbf{k}',\mathbf{r}_2)b(\mathbf{k}',\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}$$

$$-\int(b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1)b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_2)b(\mathbf{k}-\mathbf{K},\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}$$

$$+\sum_{\mathbf{k}'}\int b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}',\mathbf{r}_1)b^*(\mathbf{k}',\mathbf{r}_2)b(\mathbf{k}-\mathbf{K},\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}. \quad (15)$$

---

[12] J. C. Slater, Rev. Mod. Phys. 6, 270 (1934).

The first term represents the removal of the electrostatic interaction between the electron $\mathbf{k}-\mathbf{K}$, which is missing, with all charges, and the substitution for it of the interaction of the electron $\mathbf{k}$, which is present in its place, with all charges. The second term corrects this on account of the fact that the electron $\mathbf{k}$ must not interact with the electron $\mathbf{k}-\mathbf{K}$, which is missing. The third term removes the exchange interaction of electron $\mathbf{k}-\mathbf{K}$ with all charges. No corresponding term adding the exchange interaction of the electron $\mathbf{k}$ is present, for this electron has opposite spin to all other electrons. We now combine expressions (14) and (15), obtaining

$$
\begin{aligned}
(B(\mathbf{k}-\mathbf{K},\mathbf{k})|H|B(\mathbf{k}-\mathbf{K},\mathbf{k})) &= E_0+W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})+\sum_{\mathbf{k}'}\int b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}',\mathbf{r}_1)b^*(\mathbf{k}',\mathbf{r}_2)\\
&\times b(\mathbf{k}-\mathbf{K},\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}-\sum_{\mathbf{k}'}\sum_{\mathbf{k}''}\int\{(b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_1)b(\mathbf{k}-\mathbf{K},\mathbf{r}_1)-b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1))\\
&\times b^*(\mathbf{k}',\mathbf{r}_1)b(\mathbf{k}'',\mathbf{r}_1)\,b^*(\mathbf{k}'',\mathbf{r}_2)b(\mathbf{k}',\mathbf{r}_2)\}/\{\sum_{\mathbf{k}'''}b^*(\mathbf{k}''',\mathbf{r}_1)b(\mathbf{k}''',\mathbf{r}_1)\}2/|\mathbf{r}_{12}|d\tau_{12}\\
&-\int b^*(\mathbf{k},\mathbf{r}_1)b(\mathbf{k},\mathbf{r}_1)b^*(\mathbf{k}-\mathbf{K},\mathbf{r}_2)b(\mathbf{k}-\mathbf{K},\mathbf{r}_2)2/|\mathbf{r}_{12}|d\tau_{12}. \qquad (16)
\end{aligned}
$$

By straightforward manipulation we can express this in terms of the atomic functions. We obtain the following result, where $\mathbf{R}_0$ is the radius vector to a typical nucleus, and $\boldsymbol{\rho}$, $\boldsymbol{\rho}'$, $\boldsymbol{\rho}''$ are radius vectors from this nucleus to all others:

$$
\begin{aligned}
&(B(\mathbf{k}-\mathbf{K},\mathbf{k})|H|B(\mathbf{k}-\mathbf{K},\mathbf{k})) = E_0+W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})\\
&+\sum_{\rho,\rho'}\exp[i(\mathbf{k}-\mathbf{K})\cdot\boldsymbol{\rho}]\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\rho}-\boldsymbol{\rho}')a^*(\mathbf{r}_2-R_0-\boldsymbol{\rho}')a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}\\
&-\sum_{\rho,\rho'}(\exp[i(\mathbf{k}-\mathbf{K})\cdot\boldsymbol{\rho}]-\exp[i\mathbf{k}\cdot\boldsymbol{\rho}])\int\{[\sum_{\mathbf{R}}a^*(\mathbf{r}_1-\mathbf{R})a(\mathbf{r}_1-\mathbf{R}-\boldsymbol{\rho})]/[\sum_{\mathbf{R}'}a^*(\mathbf{r}_1-\mathbf{R}')a(\mathbf{r}_1-\mathbf{R}')]\}\\
&\times a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\rho}')a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho}')a(\mathbf{r}_2-\mathbf{R}_0)2/|r_{12}|d\tau_{12}-(1/N)\sum_{\rho,\rho',\rho''}\exp[i(\mathbf{k}\cdot\boldsymbol{\rho}+(\mathbf{k}-\mathbf{K})\cdot\boldsymbol{\rho}')]\\
&\qquad\times\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\rho})a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho}'')a(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho}'-\boldsymbol{\rho}'')2/|\mathbf{r}_{12}|d\tau_{12}. \qquad (17)
\end{aligned}
$$

It is worth while looking a little at expression (17), for it indicates the energy as given by the energy band theory, without the application of perturbations to it. The quantity $W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})$ measures the energy, as given by the energy band theory, which is necessary to take an electron from state $\mathbf{k}-\mathbf{K}$, and bring it into state $\mathbf{k}$. This of course is zero if $\mathbf{K}=0$, for then, though the spin is reversed, the electron is left in the same place in the energy band that it was before. For a small $\mathbf{K}$, the term is small, measuring the difference of energy between points separated by the vector $\mathbf{K}$ in the Brillouin zone, and can be either positive or negative depending on $\mathbf{k}$. The maximum value of the energy difference comes when $\mathbf{K}$ is the vector drawn from the point of maximum energy in the zone to the point of minimum energy, or *vice versa;* that is, ordinarily, from the center of the zone to a point on the boundary. For each value of $\mathbf{K}$, there are N states, coming from the N values of $\mathbf{k}$, and at this extreme point the N states are spread into a band whose width is twice the width of the energy band $W(\mathbf{k})$. This is indicated for a one-dimensional schematic model in Fig. 1. There we plot the band of excited levels, as a function of $\mathbf{K}$, showing that the band shrinks to zero for $\mathbf{K}=0$, increases in width proportionally to **K** for small **K**, then approaches a maximum for **K** equal to half the width of the zone (that is, the vector from the center to the edge of the zone). The whole diagram of course is periodic in **K**. Similarly in three dimensions it will be periodic with the periodicity of the reciprocal lattice.

Next we must consider the summation terms in (17). The leading term comes from the case $\boldsymbol{\varrho}=\boldsymbol{\varrho}'=0$ in the first summation, and is

$$\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0) \times a^*(\mathbf{r}_2-\mathbf{R}_0)a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}. \quad (18)$$

This measures the interaction of an electron on the typical atom with another electron on the same atom; that is, it measures essentially the energy required to take an electron from a neutral atom and put it on another atom which is already neutral, producing a negative ion, and leaving a positive ion behind. This term persists to infinite separation. Similarly the last summation of (17), for the case $\boldsymbol{\varrho}=\boldsymbol{\varrho}'=\boldsymbol{\varrho}''=0$, gives the same term, but multiplied by $-1/N$. The corresponding term of the second summation of (17) is zero on account of the cancellation of the exponential functions. All other terms of the summations in (17) involve integrals between electrons on different atoms, and hence are smaller, vanishing at infinite separation. While they cannot be neglected for all purposes, as we shall see later, we may leave them out of account in a first rough survey. We see then that added to the energy $W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})$ there is a term, approximately independent of **K**, and persisting to infinite separation, measuring $(1-1/N)$ times the work necessary to form a positive and a negative ion. The reason for this term is clear. The excited wave functions, as given by the energy band theory, correspond to an electron of negative spin traveling through the metal. The Pauli principle does not prevent it from being on the same atom with an electron of positive spin. Then it will have only one chance in N of being on the positive ion, and $(1-1/N)$ chances of being on a neutral atom, so that its average energy will include a term $(1-1/N)$ times the interaction energy with another electron on the same atom. This is a correct average result, even for infinite separation, but it is the lowest state that interests us more than the average. And the lowest state, at infinite separation, is surely that in which the electron merely reverses its spin, without moving to another atom. This state has the same energy E_0 as the initial state of maximum spin. We see therefore that while the energy band theory may be correct, and in fact proves to be correct, for the great majority of excited states, there are nevertheless a few discrete states below the continuum, which naturally are of great importance at low temperatures. We shall see later how to find more information about these discrete states.

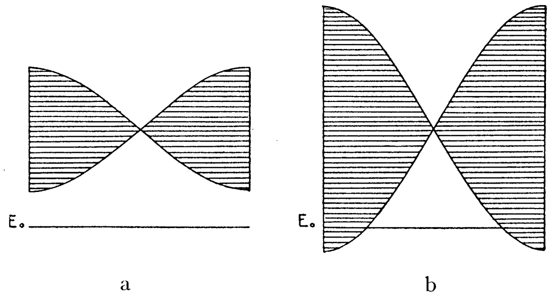

FIG. 1. Energy continuum, with one excited electron, on the energy band theory, as function of K. E_0 represents the energy of the state with all spins parallel, and the hatched areas represent the continua of excited levels. a, ferromagnetic case; b, nonferromagnetic case.

From Fig. 1, even without a study of the discrete states, we can obtain an important criterion for the existence of ferromagnetism. As far as our simple model goes, it is certainly reasonable to say that if all states with one negative spin have higher energy than the state with maximum positive spin, the system will be ferromagnetic, while if some states of negative spin have less energy than the state of maximum spin, so that the energy is reduced with reduction of net magnetic moment, the system will not be ferromagnetic. Thus a necessary and sufficient condition for ferromagnetism is that all the excited levels lie above E_0. Now the levels of Fig. 1 represent merely the average energy over unperturbed wave functions. The variation principle tells us, however, that when we find the correct wave functions and energy levels, the lowest correct energy levels will lie below the lowest unperturbed ones. As a matter of fact, there will be a set of discrete levels splitting off the bottom of the continuum, and they will necessarily lie lower than the bottom of the continuum of Fig. 1. Thus we have a necessary condition for ferromagnetism, in terms of the energy band theory: the energy bands of Fig. 1 must lie entirely above E_0, or the splitting of the energy band must be less than the interaction integral between two electrons on the same atom. This is essentially equivalent to the criterion of the references 5, though that was expressed in terms of the comparison of the state of maximum spin with that of zero spin. But this condition by itself is not sufficient. In Fig. 1a we show a case where the splitting is less than the interaction integral, so that we may have ferromagnetism; but it is still possible that some discrete states should lie below E_0, in which case the system would not show ferromagnetism. Fig. 1b, on the other hand, in which the splitting is greater than the interaction integral, represents a state which cannot possibly be ferromagnetic. In order to find more definite information about the sufficient condition for ferromagnetism, we must inquire about the discrete states.

As a next step, we shall find the energy of the excitation states $F(\mathbf{K}, \mathbf{R})$. To do this, we first need not only the diagonal but also the nondiagonal energy components in the B system. It is readily proved that there is no component of energy between two states differing in $\mathbf{K}$. Any change in the $\mathbf{k}$ value of one electron must change $\mathbf{K}$, so that the only nonvanishing components come from the simultaneous change in $\mathbf{k}$ of two electrons. We shall then compute $(B(\mathbf{k}-\mathbf{K}, \mathbf{k})|H|B(\mathbf{k}'-\mathbf{K}, \mathbf{k}'))$, in which originally there is an electron of + spin missing from state $\mathbf{k}-\mathbf{K}$, one of − spin present in $\mathbf{k}$, and finally there is one of + spin missing from $\mathbf{k}'-\mathbf{K}$, one of − spin present in $\mathbf{k}'$. Stated otherwise, the original state has an electron of − spin in state $\mathbf{k}$, and one of + spin in state $\mathbf{k}'-\mathbf{K}$, which after transition change to an electron of + spin in state $\mathbf{k}-\mathbf{K}$, and an electron of − spin in state $\mathbf{k}'$. The nondiagonal component is then given by

$$
\begin{aligned}
&(B(\mathbf{k}-\mathbf{K}, \mathbf{k})|H|B(\mathbf{k}'-\mathbf{K}, \mathbf{k}')) \\
&= \tfrac{1}{2}\sum_{\text{spin}}\int \begin{vmatrix} b_-^*(\mathbf{k}, \mathbf{r}_1) & b_-^*(\mathbf{k}, \mathbf{r}_2) \\ b_+^*(\mathbf{k}'-\mathbf{K}, \mathbf{r}_1) & b_+^*(\mathbf{k}'-\mathbf{K}, \mathbf{r}_2) \end{vmatrix} 2/|\mathbf{r}_{12}| \begin{vmatrix} b_+(\mathbf{k}-\mathbf{K}, \mathbf{r}_1) & b_+(\mathbf{k}-\mathbf{K}, \mathbf{r}_2) \\ b_-(\mathbf{k}', \mathbf{r}_1) & b_-(\mathbf{k}', \mathbf{r}_2) \end{vmatrix} d\tau_{12} \\
&\qquad = -\int b^*(\mathbf{k}, \mathbf{r}_1) b(\mathbf{k}', \mathbf{r}_1) b^*(\mathbf{k}'-\mathbf{K}, \mathbf{r}_2) b(\mathbf{k}-\mathbf{K}, \mathbf{r}_2) 2/|\mathbf{r}_{12}| d\tau_{12}. \qquad (19)
\end{aligned}
$$

Now that we have the diagonal and nondiagonal matrix components of energy in the B system, in Eqs. (16) or (17), and (19), we can readily find the components in the F system, using the transformation equation

$$
(F(\mathbf{K}, \mathbf{R})|H|F(\mathbf{K}, \mathbf{R}')) = \sum_{\mathbf{k}}\sum_{\mathbf{k}'}(1/N) \exp[i(\mathbf{k}'\cdot\mathbf{R}'-\mathbf{k}\cdot\mathbf{R})](B(\mathbf{k}-\mathbf{K}, \mathbf{k})|H|B(\mathbf{k}'-\mathbf{K}, \mathbf{k}')). \qquad (20)
$$

We find

$$
\begin{aligned}
&(F(\mathbf{K}, \mathbf{R})|H|F(\mathbf{K}, \mathbf{R}')) = E_0\delta(\mathbf{R}, \mathbf{R}') + 1/N\sum_{\mathbf{k}} \exp[i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})](W(\mathbf{k})-W(\mathbf{k}-\mathbf{K})) \\
&+\sum_{\rho} \exp[i\mathbf{K}\cdot(\mathbf{R}'-\mathbf{R})]\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0+\mathbf{R}'-\mathbf{R}-\boldsymbol{\rho})a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho})a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12} \\
&-\sum_{\rho} \exp[i\mathbf{K}\cdot\boldsymbol{\rho}]\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0+\mathbf{R}'-\mathbf{R}-\boldsymbol{\rho})a^*(\mathbf{r}_2-\mathbf{R}_0-\mathbf{R}-\boldsymbol{\rho})a(\mathbf{r}_2-\mathbf{R}_0-\mathbf{R})2/|\mathbf{r}_{12}|d\tau_{12} \\
&-\sum_{\rho}(\exp[i\mathbf{K}\cdot(\mathbf{R}'-\mathbf{R})]-1)\int \{[\sum_{\mathbf{R}_1} a^*(\mathbf{r}_1-\mathbf{R}_1)a(\mathbf{r}_1-\mathbf{R}_1+\mathbf{R}'-\mathbf{R})]/[\sum_{\mathbf{R}_2} a^*(\mathbf{r}_1-\mathbf{R}_2)a(\mathbf{r}_1-\mathbf{R}_2)]\} \\
&\qquad \times a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\rho})a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho})a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}. \qquad (21)
\end{aligned}
$$

This formula includes both diagonal and nondiagonal terms. One simplification can be made, in the second term, involving the W's. By the general theory of Brillouin zones, $W(\mathbf{k})$ is a periodic function in $\mathbf{k}$ space, and hence can be expanded in Fourier series:

$$W(\mathbf{k})=\sum_{\mathbf{R}} W_R \exp\left[-i\mathbf{k}\cdot\mathbf{R}\right], \tag{22}$$

where the summation is over all vectors $\mathbf{R}$ from a typical atom to all other atoms. Using this expansion, we find easily

$$1/N\sum_{\mathbf{k}} \exp\left[i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})\right](W(\mathbf{k})-W(\mathbf{k}-\mathbf{K}))=W_{\mathbf{R}'-\mathbf{R}}(1-\exp\left[i\mathbf{K}\cdot(\mathbf{R}'-\mathbf{R})\right]). \tag{23}$$

Just as with the energy band functions, it is interesting to consider the diagonal energy in terms of the F functions. Since the formulas simplify considerably when $\mathbf{R}'-\mathbf{R}=0$, it is worth while writing these diagonal terms:

$$\begin{aligned}(F(\mathbf{K},\mathbf{R})|H|F(\mathbf{K},\mathbf{R}))=E_0&+\sum_{\rho}\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\varrho})a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\varrho})a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}\\ &-\sum_{\rho}\exp\left[i\mathbf{K}\cdot\boldsymbol{\varrho}\right]\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\varrho})a^*(\mathbf{r}_2-\mathbf{R}_0-\mathbf{R}-\boldsymbol{\varrho})a(\mathbf{r}_2-\mathbf{R}_0-\mathbf{R})2/|\mathbf{r}_{12}|d\tau_{12}.\end{aligned} \tag{24}$$

The leading terms come from the case $\boldsymbol{\varrho}=0$. Then the first summation represents the potential of an electron on the atom at $\mathbf{R}_0$, on itself, while the second summation is the potential of an electron on R_0, on another electron on the atom at $\mathbf{r}_0+\mathbf{R}$. If $\mathbf{R}=0$, these terms just cancel, so that the energy is E_0, except for exchange terms with neighboring atoms, which we shall consider in a moment. If $\mathbf{R}\neq 0$, on the other hand, the terms do not cancel, but instead the second reduces approximately to the potential between a spherical charge on the atom at $\mathbf{R}_0$, and a spherical charge on the atom at $\mathbf{R}_0+\mathbf{R}$, which is $2/|\mathbf{R}|$. That is, the whole thing reduces to the energy necessary to form a positive and negative ion at distance $\mathbf{R}$, the Coulomb term $-2/|\mathbf{R}|$ arising from the attraction of the ions for each other. To this approximation, we shall have a series of N terms for each $\mathbf{K}$ value, the lowest one being approximately E_0, the others converging, as $\mathbf{R}$ becomes large, to a limit. Since most of the terms lie arbitrarily close to the limit, the average energy of the terms is closely equal to the limit, and by general principles of wave mechanics this average value must also equal the average value of the terms as computed in Fig. 1 from the energy band theory.

We shall now consider these states in more detail. The lowest state is for $\mathbf{R}=0$, and for it we have

$$\begin{aligned}(F(\mathbf{K},0)|H|F(\mathbf{K},0))=E_0&\\ +\sum_{\rho}(1-\left[\exp i\mathbf{K}\cdot\boldsymbol{\varrho}\right])&\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\varrho})\\ &\times a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\varrho})a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}.\end{aligned} \tag{25}$$

The integral in (25) is the interaction of a charge distributed on atoms $\mathbf{R}_0$ and $\mathbf{R}_0+\boldsymbol{\varrho}$, on itself, and hence is necessarily positive. Furthermore it is equal for all neighbors $\boldsymbol{\varrho}$ at a fixed distance from $\mathbf{R}_0$, and falls off rapidly as $\boldsymbol{\varrho}$ increases, so that for approximate purposes we need consider only nearest neighbors. The factor $(1-\exp i\mathbf{K}\cdot\boldsymbol{\varrho})$ is zero for $\mathbf{K}=0$, showing that the energy of this state is exactly E_0 at the center of the zone, but is positive for other $\mathbf{K}$'s, showing that the energy increases for other $\mathbf{K}$ values, reaching a maximum at the edge of the zone. This behavior is shown in Fig. 2, where these energy levels are

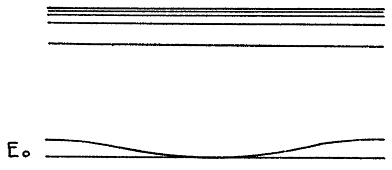

FIG. 2. Energy levels with one excited electron, on the spin wave theory, as function of K.

plotted as functions of $\mathbf{K}$, in the same way that the energy band levels were plotted in Fig. 1. This variation with $\mathbf{K}$ is just what Bloch found for his spin waves, which are essentially equivalent to our functions $F(\mathbf{K}, 0)$, with one exception: the exchange integral which Bloch had was the Heisenberg exchange integral, involving both a positive term, coming from interaction of the electrons with each other, and a negative term, coming from interaction with the nuclei. Thus if the positive term were larger than the negative, the energy of the spin wave would be larger than E_0 for all $\mathbf{K}$'s except $\mathbf{K}=0$, leading to ferromagnetism, while if the negative term outweighed the positive one, the energy would be less than E_0, and there would be no ferromagnetism. We have at this point only the equivalent of his positive term, and shall find that the negative contribution is supplied later when we perform our perturbation calculation. As for the states with $\mathbf{R}\neq 0$, the variation with $\mathbf{K}$ is unimportant. It comes from the last summation in Eq. (24). This represents the interaction between a charge shared on atoms $\mathbf{R}_0$ and $\mathbf{R}_0+\boldsymbol{\rho}$, on a similar charge displaced a distance $\mathbf{R}$. Now on account of the orthogonality of the a's, the net charge in one of these distributions must be zero, so that it is a multipole. On account of symmetry it cannot be a dipole, and must be at the least a quadripole. Thus we have the potential of a quadripole on another, falling off as a high inverse power of the distance, and becoming practically negligible after the distance $\mathbf{R}$ becomes appreciable. Thus the higher states in Fig. 2 are drawn independent of $\mathbf{K}$.

The Perturbation Problem

We have now derived the matrix components of energy in two systems, and we can proceed from either one to set up the perturbation problem to get the actual states of the system. If we start with the energy band picture, as in Fig. 1, we shall find that the perturbations split certain discrete levels from the continuum, leaving the major part of the continuum essentially unchanged. If we start on the other hand from the functions of Fig. 2, where the lowest state represents the spin waves, and the higher states represent polar spin waves, the perturbation will spread out the large number of levels near the series limit into a band or continuum, at the same time distorting the lower levels, and in general depressing them. The result of either sort of calculation is the same, and is indicated in Fig. 3, where in 3a we see the case where all of the final states lie above E_0, so that we have ferromagnetism, while in 3b some of the levels lie below E_0, so that the energy of the system can be decreased by reducing the net magnetic moment, and we do not have ferromagnetism. In either case it is the perturbed spin wave level, the one corresponding to $F(\mathbf{K}, 0)$, which results in the lowest level. If this lies above E_0 for all $\mathbf{K}$'s, we have ferromagnetism, and otherwise not. We shall therefore study this state in detail.

It is easiest to study this spin wave in terms of the functions F, using the matrix components in (21). We first consider the point $\mathbf{K}=0$. The unperturbed energy for this value of $\mathbf{K}$ is just E_0, as we saw from Eq. (25). Furthermore, an examination of (21) shows at once that the nondiagonal components from this state to other states, $(F(0, 0)|H|F(0, \mathbf{R}'))$, are all zero. Thus the function $F(0, 0)$, with the energy E_0, is an exact solution of the problem, and the lowest energy level must go through the point $\mathbf{K}=0$, energy $=E_0$, possessing a minimum or maximum there by symmetry. As a matter of fact, we can show by a perfectly general argument that there must be a state of the system with these values of $\mathbf{K}$ and energy. For out of all the N^2 states corresponding to a component of spin along the axis connected with $(N-1)$ parallel spins, 1 antiparallel spin, there must be (N^2-1) states corresponding to the same total spin, and 1 state corresponding to the particular orientation of the state of maximum spin (N parallel spins) which has a component corresponding to $N-1$ spins along the axis. This one state must, by the general theory of multiplets, have the same energy E_0 and the same value $\mathbf{K}=0$ characteristic of the state of maximum spin, which we are using as our zero of reference. Thus this level with $E=E_0$ is not really a level of the problem we are considering at all, and we could have predicted its existence from the outset. We could not, however, have predicted on general grounds that other levels should join smoothly onto this level.

We next consider the nondiagonal matrix components $(F(\mathbf{K}, 0)|H|F(\mathbf{K}, \mathbf{R}))$ between the lowest state and other states, when $\mathbf{K}\neq 0$. The leading term is the one given in (23), equal to $W_R(1-\exp i\mathbf{K}\cdot\mathbf{R})$. The other terms, in the summations, are all exchange terms between neighbors, and so are small. Furthermore, even the leading term in the summations cancels. This is the term $\boldsymbol{\rho}=0$. In the last summation of (21), in this case, the most important contributions to the summations over $\mathbf{R}_1$ and $\mathbf{R}_2$ come by setting $\mathbf{R}_1=\mathbf{R}_2=\mathbf{R}_0$. If this is done, and $\boldsymbol{\rho}=0$, it is easy to see that the summations vanish. The remaining terms are small enough so that we can safely neglect them. Thus we are left only with the nondiagonal term $W_R(1-\exp i\mathbf{K}\cdot\mathbf{R})$. We may expect that W_R is largest for interactions with nearest neighbors, $\mathbf{R}$ = distance from an atom to its nearest neighbor. In fact, if $W(\mathbf{k})$, in (22), is given by the formula of Bloch's approximate theory, the interaction W_R is zero except for nearest neighbors, negative for nearest neighbors. Thus we may expect to get a good approximation if we consider only interactions of $F(\mathbf{K}, 0)$ with those functions in which the electron of negative spin is removed to a nearest neighbor of the atom from which it has come.

It is not practical to try to get exact solutions for the lowest state of the real system, so we shall first proceed by perturbation theory. Using second-order perturbations, and considering interactions with nearest neighbors, as we have just stated, we then have

$$\text{energy}=(F(\mathbf{K},0)|H|F(\mathbf{K},0))-\sum_{\mathbf{R}}W_R{}^2\frac{(1-\exp[i\mathbf{K}\cdot\mathbf{R}])(1-\exp[-i\mathbf{K}\cdot\mathbf{R}])}{E(\mathbf{R})-E(0)}. \qquad (26)$$

Here $E(\mathbf{R})$ is the unperturbed energy of the $\mathbf{R}$ state, $(F(\mathbf{K}, \mathbf{R})|H|F(\mathbf{K}, \mathbf{R}))$, and $E(0)$ is the energy of the 0 state, $(F(\mathbf{K}, 0)|H|F(\mathbf{K}, 0))$. Since $E(\mathbf{R})$, W_R are the same for all nearest neighbors $\mathbf{R}$, we can take them out of the summation. We shall adopt two abbreviations: in (25), we let the integral be I_0:

$$I_0=\int a^*(\mathbf{r}_1-\mathbf{R}_0)a(\mathbf{r}_1-\mathbf{R}_0-\boldsymbol{\rho})a^*(\mathbf{r}_2-\mathbf{R}_0-\boldsymbol{\rho})\times a(\mathbf{r}_2-\mathbf{R}_0)2/|\mathbf{r}_{12}|d\tau_{12}, \qquad (27)$$

where $\boldsymbol{\rho}$ is the vector to one of the nearest neighbors. Secondly, we let

$$I_1=E(\mathbf{R})-E(0). \qquad (28)$$

Furthermore, we shall neglect the fact that I_1 depends on $\mathbf{K}$, since the dependence, which comes from $E(0)$, is not very great. We remember that the largest term in I_1 is the energy of interaction between two electrons on the same atom, a fairly large quantity compared with the variation of $E(0)$ with $\mathbf{K}$. Then in evaluating (26), we must first find the summation $\sum_\rho(1-\exp i\mathbf{K}\cdot\boldsymbol{\rho})$ from (25). The exponential can be written as $\cos\mathbf{K}\cdot\boldsymbol{\rho}+i\sin\mathbf{K}\cdot\boldsymbol{\rho}$, of which the second term is odd in $\boldsymbol{\rho}$. Now for each neighbor there will be another diametrically opposite, so that the sine terms will cancel in pairs, leaving only the cosine terms. Hence

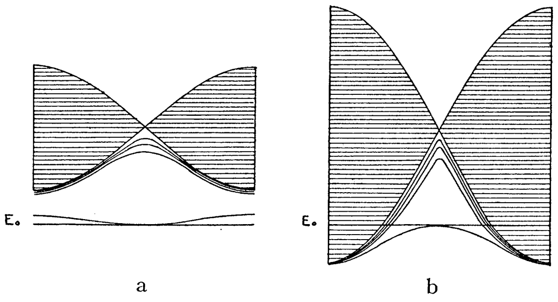

FIG. 3. Energy levels with one excited electron, as function of K, as result of perturbation theory applied to methods of Fig. 1 or Fig. 2. a, ferromagnetic case; b, nonferromagnetic case. Note: Figs. 1, 2, 3 are merely schematic, not the result of actual computations.

$$\sum_\rho(1-\exp[i\mathbf{K}\cdot\boldsymbol{\rho}])=\sum_\rho(1-\cos\mathbf{K}\cdot\boldsymbol{\rho}). \qquad (29)$$

Also we must work out the sum in (26). This is

$$\sum_{\mathbf{R}}(1-\exp[i\mathbf{K}\cdot\mathbf{R}])(1-\exp[-i\mathbf{K}\cdot\mathbf{R}])=\sum_{\mathbf{R}}2(1-\cos\mathbf{K}\cdot\mathbf{R}), \qquad (30)$$

twice the previous summation. Thus we have

$$\text{energy of lowest state}=E_0+A\sum_{\mathbf{R}}(1-\cos\mathbf{K}\cdot\mathbf{R}),$$

where

$$A=I_0-2W_R{}^2/I_1. \qquad (31)$$

The formula (31) gives a variation with $\mathbf{K}$ just like Bloch's solution for the same spin wave, as we have mentioned above. Now, however, we get more complete agreement with the Bloch or Heisenberg type of theory, in which A would take the place of the interaction or exchange integral between neighbors. For now our integral A is made up of two parts, a positive and a negative one, the positive one coming from electrostatic interactions between electrons, the negative one from the splitting of the energy band, which amounts to interactions between electrons and nuclei. Plainly the quantity A can be of either sign, and if it is positive we have ferromagnetism, otherwise not. (We must remember that our formula, being derived from perturbation theory, is not very accurate for large perturbations, or large W_R. Thus it should be fairly good for the ferromagnetic case, but inaccurate for the nonferromagnetic case.) It is interesting to consider how A will change as the energy band broadens. Both I_0 and W_R depend on the overlapping of neighboring atoms, though in a rather independent way. For purposes of orientation, we may suppose that they are proportional to each other: $I_0=\alpha|W_R|$, where probably α is considerably smaller than unity. Then we have

$$A=\alpha|W_R|-2W_R^2/I_1, \qquad (32)$$

a quadratic in W_R, going to zero when $W_R=0$, rising to a maximum as the overlapping increases, then going to zero again when $|W_R|=\alpha I_1/2$, finally becoming and staying negative. This is the behavior which has often been discussed, in which ferromagnetism starts weakly with small overlapping of neighbors (as in the rare earths), increases with greater overlapping (as in the iron group), then disappears with still more overlapping (as in the conduction electrons of nonferromagnetic elements).

A more accurate solution of our perturbation problem can be obtained in some special cases. Thus consider a body centered lattice, and let **K** be at the edge of the band. That is, **K** is along one of the three axes, and its magnitude is such that $\cos \mathbf{K}\cdot\mathbf{R}=-1$ for each of the eight neighbors. Our problem is then to find combinations of all functions $F(\mathbf{K},\mathbf{R})$, for all **R**'s, which will be solutions of the problem. Remembering that each atom has eight neighbors, the diagonal energy of the state $F(\mathbf{K},0)$ is E_0+16I_0. To the approximation which we have been making, we can set the diagonal energy of all other states $F(\mathbf{K},\mathbf{R})$ for $\mathbf{R}\neq 0$ equal to E_0+I_1. Furthermore, the nondiagonal matrix component from one function to any one of its eight nearest neighbors is $2W_R$, and to any further neighbor we assume it to be zero. By symmetry, the lowest state will then have a wave function in which all functions with the same magnitude of **R**, but different directions, will have the same coefficient. Thus let the function $F(\mathbf{K},0)$, the nonpolar function, have the coefficient C_0. The next more distant functions, corresponding to the removal of the electron to one of the eight nearest neighbors, at $(\pm 1, \pm 1, \pm 1)$ times the lattice spacing, will have the coefficient C_1. The six functions connected with the next nearest neighbors $(\pm 2, 0, 0)$, $(0, \pm 2, 0)$, $(0, 0, \pm 2)$, will have the coefficient C_2. We continue in this way. Then it is easy to set up the secular equation for the energy. This is found, by consideration of the number of neighbors of each type which each function has, to be the following:

$$\begin{vmatrix} E_0+16I_0-E & 16W_R & 0 & 0 & 0 \\ 2W_R & E_0+I_1-E & 6W_R & 6W_R & 0 \\ 0 & 8W_R & E_0+I_1-E & 0 & 8W_R \\ 0 & 4W_R & 0 & E_0+I_1-E & 4W_R \\ 0 & 0 & 2W_R & 4W_R & E_0+I_1-E \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{vmatrix}=0. \qquad (33)$$

We can approximate this successively by a quadratic (using the four elements in the first two rows and columns), a cubic, quartic, etc., using successively more rows and columns. This has been done, carrying it up to the fifth degree equation, which amounts to using the nonpolar state and the four nearest sets of neighbors. In Fig. 4 the results are plotted for each of these approximations, as well as for the second order perturbation method of Eq. (31). The integral I_1 in Fig. 4 is taken as the unit of energy, and the quantity $16|W_R|$ is used as the abscissa, so that the figure shows what happens as the energy band becomes broader and broader. The straight line represents $I_1-16|W_R|$, which is easily seen to be the bottom of the Bloch continuum, in case the zero of energy represents E_0. The point where it crosses the axis is the point where the theory of energy bands would indicate that ferromagnetism ceased. The various curves, all approximations to one correct solution of the perturbation problem, indicate the lowest stationary state of the problem, essentially Bloch's spin wave, as it is determined from the secular Eq. (33). For $W_R=0$, this reduces simply to E_0+16I_0, and we have shown the case where $16I_0=1/10I_1$. That is, we have assumed the interaction integral of the electron with its neighbors $(16I_0)$ to be one-tenth the interaction with a similar electron on the same atom (I_1). This seems like a reasonable assumption in the ferromagnetic case.

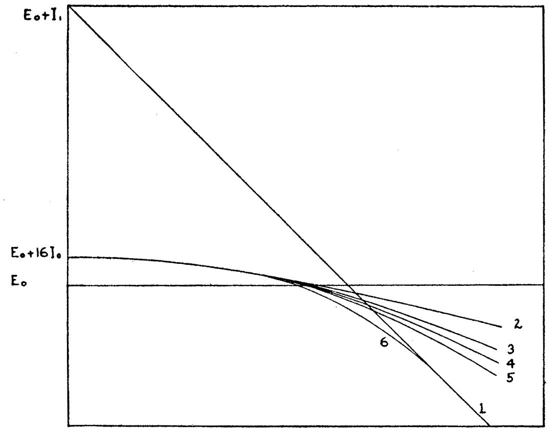

FIG. 4. Various approximations to the lowest energy level, as function of W_R, the width of the energy band. Straight line (1) represents the bottom of the energy continuum. Curves (2), (3), (4), (5), are solutions of the second, third, fourth, and fifth power secular equations approximating the Eq. (33). Curve (6) represents the solution of Eq. (36). The second order perturbation approximation of Eq. (31) lies very close to curve (2).

Still another approximation curve is shown in Fig. 4, lying lower than the others, and therefore still nearer the truth. This was obtained by a method similar to Wannier's operator method.[10] Let us suppose that the coefficients C vary slowly from one atom to its neighbors. We shall now label the C's with the indices of the atom to which they refer: $C(n_1n_2n_3)$ is the coefficient of the function $F(\mathbf{K},\mathbf{R})$ for which the vector $\mathbf{R}$ equals (n_1, n_2, n_3) times the lattice spacing. Then, so long as $n_1n_2n_3$ is neither the central atom, $\mathbf{R}=0$, nor one of its eight nearest neighbors, the corresponding Eqs. (33) all reduce to the form

$$\begin{aligned}(E_0+I_1-E)&C(n_1n_2n_3)\\&+2W_R(C(n_1+1,\ n_2+1,\ n_3+1)+\cdots\\&\qquad+C(n_1-1,\ n_2-1,\ n_3-1))=0,\end{aligned}\tag{34}$$

where there are eight terms multiplying $2W_R$. Now suppose that we can expand the C's in power series in the n's, and break off with second power terms, which we can do if the C's vary sufficiently slowly. The linear terms will vanish, equal and opposite contributions coming from opposite neighbors. We are then left only with terms coming from the second derivatives. These give the equation

$$\begin{aligned}(E_0+I_1+16W_R-E)C(n_1n_2n_3)+8W_R(\partial^2/\partial n_1^2\\+\partial^2/\partial n_2^2+\partial^2/\partial n_3^2)C(n_1n_2n_3)=0.\end{aligned}\tag{35}$$

Eq. (35) is the wave equation, and we find the desired spherically symmetrical solution by assuming

$$\begin{aligned}C(n_1n_2n_3)=(\exp\ -\alpha(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}})\\/(n_1^2+n_2^2+n_3^2)^{\frac{1}{2}}.\end{aligned}\tag{36}$$

where α is an arbitrary constant. Between α and the energy there must exist the relation

$$E=E_0+I_1+16W_R+8W_R\alpha^2.\tag{37}$$

Eq. (37) has a simple interpretation in terms of Fig. 4. Remembering that W_R is negative, we see that $E_0+I_1+16W_R$ represents the straight line of Fig. 4, or the bottom of the energy band continuum. Eq. (37) then says that the energy E lies below this energy, by an amount which is smaller, the smaller α becomes. Small α corresponds to a wave function which is reduced only very slowly as $(n_1^2+n_2^2+n_3^2)$ increases; that is, to a very extended wave function.

The expression (36) clearly cannot be used for $n_1=n_2=n_3=0$, for it then becomes infinite. Let us then assume (36) for all other values of the n's, and assume an independent value C_0 for the central atom. We then have three variables, C_0, α, and E, and we must find three equations to determine them. One of these equations is (37), and it is natural to take as the other two the first two equations of those indicated in the determinant (33), so that the relations will be exactly satisfied for the central atom and its next nearest neighbors. Eliminating C_0, these give a relation between the energy and α which can be easily solved, and the result is plotted in Fig. 4. As we see, the energy of the state gradually approaches the bottom of the continuum, with corresponding decrease of α, or increase of the size of the wave functions. Even this solution proves not to be good for very large values of W_R; the solution shows a curious behavior by which α becomes zero for a finite value of W_R, which surely does not correspond to the real behavior. It is safe to say, however, that this solution is fairly near the truth in the region where it lies above the energy E_0, which is the ferromagnetic case, and that it indicates the correct trend even when it lies below E_0.

The situation, then, as indicated by Fig. 4 and the calculations leading up to it, is the following. The energy band of Figs. 1 and 3, as it increases in width, pushes the lowest wave function down, and it pushes it below E_0, destroying ferromagnetism, when the energy band is about eighty percent of the integral I_1, rather than one hundred percent as in the elementary energy band theory. This numerical value, of course, represents a special case, but it probably indicates the order of magnitude to be expected in general. Until the band is almost of this width, the simple second order perturbation calculation of Eq. (31) represents the energy quite accurately, and can be used safely in the ferromagnetic case. The wave function in this case consists of a mixture of the function $F(\mathbf{K}, 0)$ and the functions $F(\mathbf{K}, \mathbf{R})$ in which $\mathbf{R}$ is the nearest neighbor to the central atom. We remember that $F(\mathbf{K}, 0)$ is a function in which an electron is removed from a certain atomic function, its spin is reversed, and then it is replaced in the same atomic function. Finally all such functions are combined to make a wave of spin traversing the metal. But the atomic function, being one of the orthogonal functions, is not really confined entirely to one atom, but has appreciable values on nearest neighbors, so $F(\mathbf{K}, 0)$ contains an appreciable probability that the reversed electron will be found on a nearest neighbor. $F(\mathbf{K}, \mathbf{R})$ consists largely of the probability that the reversed electron will be on the nearest neighbor, and it enters with such a sign as partly to cancel the probability of being on the neighbor already present in $F(\mathbf{K}, 0)$. In other words, the final wave function is one in which the reversed electron is almost sure to be on the atom from which it originally came, rather than forming an ion by shifting to its neighbor. This is essentially the wave function of the Heisenberg theory, made of nonorthogonal functions, though doubtless there will be some small amount of polar function left in it. Our final result, then, is in close agreement with the atomic type of theory, as far as the lowest stationary state in the ferromagnetic case is concerned.

In the other limit, however, when the width of the energy band, W_R, becomes large, our solution departs widely from the atomic type. In the first place, the energy levels of the discrete states draw in very closely to the bottom of the continuum, so that the energy band method becomes very accurate for a calculation of energy. In the second place, as we see from the type of solution (36), the wave function changes its character entirely. It is a combination of many $F(\mathbf{K}, \mathbf{R})$'s, corresponding to large $\mathbf{R}$ values, with coefficients which fall off slowly with the magnitude of $\mathbf{R}$. That is, it is a wave function in which the electron is only tied loosely to the positive ion which it has left behind, and wanders at considerable distances from it through the crystal, though not reaching infinite distance. Our solution unfortunately is not accurate enough to give exact values for the size of this wave function. In a qualitative way, however, it is similar to those found by Wannier[10] in a similar problem. The equations (34) of course have other, higher solutions, in addition to the one we have found, which would be analogous to the 1*s* state of a hydrogen atom. There will be a series of *s*-like states, in which all neighbors at a given distance have the same coefficients, and in which the C's can be determined approximately from the differential equation (35).

Then there will be solutions of different symmetry, corresponding to p, d, $\cdots$ states of the hydrogen atom. These will form a series of discrete levels, which may have a larger or smaller total number of levels according to circumstances, lying between the lowest level, which we have investigated, and the continuum. And the size of the wave function will grow larger and larger, as we go to higher and higher "quantum numbers," regarding the wave function as sort of an "atom" on a large scale. It is this type of solution which is of importance in nonferromagnetic substances, and which we discuss in connection with the problem of superconductivity in the following paper.[13]

CONCLUSION

Starting with the theory of energy bands, we have set up the perturbation problem and solved approximately the case of a band containing half enough electrons to fill it, all having parallel spins but one. This problem is a test for ferromagnetism: if the lowest energy of the problem is lower than the energy when all have parallel spins, the system will tend to reduce its spin, and will not be ferromagnetic, whereas if all energies of the problem are higher than the state of maximum spin, the latter will be the stable state, and we shall have ferromagnetism. On the theory of energy bands, applied in an elementary way, as in reference 5 on the ferromagnetism of nickel, the lowest state of this problem of $(N-1)$ positive spins is found by taking the electron of positive spin from the top of the band, introducing it with negative spin at the bottom of the band, thereby reducing the energy a good deal. This reduction of energy is partly counterbalanced by the exchange integral, an interaction between an electron and another on the same atom, which increases the energy when the spin is reversed. If the energy reduction on account of the energy band is less than the exchange integral, there will be ferromagnetism, otherwise not. When we carry out our present more refined calculation, we find that in broad outlines this criterion is still a correct one. We find, however, that there are discrete energy levels below the continuum given by the energy band theory, and that some of these may lie below the energy of the state of maximum spin, destroying ferromagnetism, even when the elementary theory would predict ferromagnetism. These discrete states are states in which the electron of negative spin stays on or in the immediate neighborhood of the atom to which it formerly was attached with positive spin. When it had positive spin, the Pauli principle prevented it from passing to neighboring atoms, since they already had similar electrons. This prohibition is removed when the spin reverses, and the only thing holding the electron to its atom is now electrostatic action, or the correlation energy between the electron and positive ion. The energy by which the lowest discrete level lies below the continuum is a measure of the correlation energy. When we consider this correlation energy, we find that ferromagnetism will be destroyed when the reduction of energy on account of the width of the energy band is something like eighty percent of the exchange integral, the difference being made up by the correlation energy. Thus the criterion is changed quantitatively, but not qualitatively.

The lowest energy level of the system, the correlation state just described, is equivalent to the spin wave of Bloch's theory, and makes direct connection with Heisenberg's formulation of ferromagnetism. But we have described it in terms of orthogonal functions and energy bands, gaining in mathematical simplicity by the elimination of nonorthogonality integrals, and making connection with other parts of the theory of metals. At low temperatures, and perhaps at ordinary temperatures, it will be this spin wave which is excited, and probably the higher waves in the continuum will not be excited. Thus Bloch's deduction of the temperature variation of the magnetic moment at low temperatures, based on spin waves, should be correct, and a deduction based on the levels in the continuum is probably not valid.

In the nonferromagnetic case, where the energy bands are broad, there are still separated, discrete levels, but they approach closer and closer to the continuous band as it broadens. At the same time the wave function changes, becoming more and more extended. Instead of corresponding closely to a spin wave, the lowest state describes an electron which wanders far

---

[13] J. C. Slater, Phys. Rev. (following paper, this issue).

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.

The writer wishes to thank Professor J. H. Van Vleck for valuable discussions of the subject of this paper. He also wishes to thank the Institute for Advanced Study for the privilege of conducting these investigations in residence at Princeton.

AUGUST 1, 1937 PHYSICAL REVIEW VOLUME 52

The Nature of the Superconducting State. II

J. C. Slater
*Institute for Advanced Study, Princeton, New Jersey**

(Received May 7, 1937)

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

---

* On leave from the Massachusetts Institute of Technology, Cambridge, Mass.

[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).