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COHESION IN MONOVALENT METALS

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Abstract

The theory of metallic structure, of Sommerfeld, Heisenberg, and Bloch, is carried far enough to explain cohesive forces, and calculations are made for atoms with one valence electron, particularly metallic sodium. The numerical results, though rough, are in qualitative agreement with experiment. It is found that the forces in general are of the same nature as those met in ordinary homopolar binding, discussed by Heitler and London; except that the purely electrostatic force from penetration of one atom by another is relatively more important, the valence effect from the exchange of electrons relatively less important, than in diatomic molecules.

As a preliminary to the calculation, the relations of the methods of Heisenberg and of Bloch are discussed, and it is shown that they are essentially equivalent in their results when properly handled. Remarks are made both about conductivity and ferromagnetism. In connection with conduction, it is shown that a definite meaning can be given to free electrons, that they are necessary to conduction, and that a method can be set up for computing their number, which is rather small compared with the number of atoms. Ferromagnetism is discussed in connection with a recent paper of Bloch. It is shown that a metal like an alkali cannot be ferromagnetic, for atoms at such a distance that the interatomic forces keep the metal in equilibrium, are too close to be magnetic. For ferromagnetism, rather, it seems necessary to have one group of electrons responsible for cohesion, and another group, of smaller orbit and therefore relatively farther apart, producing the magnetism; a situation actually found only in the iron group and the similar groups.

I. Introduction

A crystal of a metal is an enormous molecule, with electronic energy levels depending on the positions of all the nuclei, just as the electronic energy of a diatomic molecule depends on the internuclear distance. In this paper, in which we are interested in cohesive forces, we must find this energy of the lowest state in terms of the size of the crystal. We limit ourselves to geometrically similar arrangements of the nuclei, with changing scale. From the minimum of the curve, we find the heat of dissociation, grating space, and compressibility of the metal. But also we can investigate the wave function of this lowest state, and obtain information about the electric and magnetic properties of the metal. In this way we are naturally led to a discussion of the calculations of Heisenberg[1] and of Bloch on these subjects; in order to be sure that we really understand the arrangement of energy levels, we discuss the relationships of their methods, and arrive at a consistent picture combining them.

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[1] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928);
F. Bloch, *ibid.* **52**, 555 (1929).

As for the results, one naturally asks first, what are the forces holding a metal together? Are they ordinary attractions on account of penetration of atoms, or valence forces, or electrostatic forces of ionic attraction, or van der Waals forces, or some special sort not found in other cases? This question cannot be answered categorically; no doubt all the forces are simultaneously present, and the problem is to find the relative magnitudes. The tentative result at which we arrive is that the simple penetration of one atom by another is the most important part of the effect. But valence effects are also present, although weakened by having the valences shared by many neighbors, and are responsible for a considerable fraction of the attraction. Although these actual magnitudes may not be verified by more accurate calculation, still we have discussed the problem in enough detail so that the general relations can be understood in any case.

The other question one will ask is, what is the situation of the electrons in the metal? Can one give a meaning to the question, how many free electrons are there? The answer, from whichever side we look at the question, seems to be the same. Most of the valence electrons are at any time attached to their atoms. These electrons cannot take part in conduction; they could do it only by having a whole file of such electrons simultaneously jump to the next atom in line, a most unlikely occurrence. But a few electrons at any time—calculation suggests a few percent—will be detached from their atoms, leaving an equal number of positive ions behind them; and they are what, by all rights, one should call free electrons. These electrons, and the positive ions left behind, can take part in conduction. First, the free electrons can move easily from one atom to the next. Second, a bound or associated electron on one of the atoms next a positive ion can jump to that ion, leaving its own atom ionized. We are thus led precisely to the dual theory of conduction, by free and by associated electrons, which Professor Hall[2] has suggested and elaborated. When we look at the metal by the method of Heisenberg, these results become clear. In that method, a wave function consists of the assignment of electrons to atoms. We find that we must go beyond Heisenberg, in assigning sometimes two electrons to one atom, sometimes none, instead of always one; for we need such states to solve the problem of the stationary states of the metal. That is, we introduce free electrons. And when we consider transitions from one state to another, it is easy to see that these transitions can result in conduction only when such free electrons are present. On Bloch's scheme, where we describe directly the velocity, rather than the position, of the electrons, it is less easy to see the relation; but here too one can show that, if there are no free electrons, the velocities of all electrons must compensate, so that there is no net current. Since this paper is not primarily about conduction, we do not go into these points with any detail.

The only metals specifically treated are those with one valence electron per atom, and that in an *s* state; that is, the alkalies. And it is assumed that they can be replaced by single valence electrons moving in non-coulomb

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[2] E. H. Hall, Proc. Nat. Acad., 1920–1921.

fields. This can be easily justified. It is to be noted that the other metals are more complicated, not merely by having more electrons, but by having them in p or d orbits, thus introducing new degeneracies. The actual calculations of cohesion have been carried through for sodium, with satisfactory results. They are only done roughly, however; the primary purpose of this paper is to make clear the general relations, rather than to attempt accurate calculations. The work is being carried further by Dr. Bartlett, and I wish to thank him for help on some of the calculations used in this paper. The work described here has been done while the writer was on leave, working in Leipzig. He wishes to thank Professor Heisenberg for his courtesy in extending the privileges of his laboratory, and for a number of illuminating conversations on the subject of the paper; and also to thank Harvard University for granting leave, and the Guggenheim Foundation for the assistance of a fellowship.

2. Comparison of Heisenberg's and Bloch's Methods

The problem of a metal must be attacked by perturbation theory, and the unperturbed functions which we use can be set up in two quite different ways, one used by Heisenberg, the other by Bloch, either giving us a finite set of unperturbed functions. We regard the perturbation problem in the following way: we seek those linear combinations of these functions which, in the sense of the variation method, form the best approximations to solutions of Schrödinger's equation. This problem is solved by computing the matrix of the energy operator with respect to these functions, and solving the equations

$$\sum_k (H(i/k) - \delta(i/k)W)S(k) = 0$$

for the coefficients $S(k)$ to be used in making the linear combinations, and the energy values W of the resulting terms. (The term $\delta\ (i/k)$ must be given a slightly different form if the unperturbed functions are not orthogonal). This differs from the more conventional method: there one starts with an infinite, complete set of unperturbed functions, instead of our finite set, but solves only as a power series in the non-diagonal terms of the energy matrix, breaking off after the second power in all ordinary applications. It resembles more closely the quite different method ordinarily used with degenerate systems, where one takes only very few unperturbed states, but correctly solves the problem of combining them. For a nearly degenerate problem like the present one, with a great many states near together, the conventional method of developing in series will not work well, for the series do not converge well, and we are forced to use something like the present method. The justification comes simply from the assumption that the lowest states can be well approximated by such a linear combination of Heisenberg's or Bloch's functions (which correspond to having the atoms in their normal states). Surely this is not exact; for better results we should have to consider also the excited states of the atoms. But also certainly it is a fair approximation for the lowest states of the metal.

Heisenberg's functions, amplified in a simple way, form good approximations when the crystal is extended, for they are derived from the separated atoms. Bloch's functions on the other hand come by analogy with the free electron theory of Sommerfeld, and are good approximations when the crystal is compressed. The actual solutions of the perturbation problem are of course linear combinations of either Heisenberg's or Bloch's functions, not individual ones, and one gets the same final result whichever set one starts with (for the two sets of functions can be written as linear combinations of each other). But the fact that in the limiting cases the functions of one of the two sets become rather good approximations can be used, along with interpolation, to derive the general nature of the real stationary states. This comparison is made in the present section, and is illustrated by the interesting case of H_2, where the calculations can be made exactly. At the outset, we must recognize two facts: first, that we must amplify Heisenberg's method by including polar states, to make it general enough to agree with Bloch's and to permit conductivity; second, that although Bloch has the proper set of functions, he has nowhere attempted to solve the perturbation problem, but has merely taken his unperturbed functions as being correct, which amounts to getting the energy to the accuracy of the conventional "first order perturbations."

The first step in either Heisenberg's or Bloch's method, as we apply them, is to write an approximate solution as a product of functions of the individual electrons. Heisenberg takes, for these separate functions, the wave functions of electrons attached to individual nuclei; the number of such functions is the product of the number of nuclei, multiplied by the number of different sets of quantum numbers we consider for an individual nucleus. If we restrict ourselves to s states, there are then only two states per nucleus, corresponding to the two orientations of the spin. For nucleus a, we denote these two[3] by $u_\alpha(a/x)$, $u_\beta(a/x)$, and we have such a function for each nucleus $a\ b\ .\ .\ .\ n$. Bloch takes, on the other hand, combinations of these functions:

$$u_\alpha(klm/xyz)=\sum_{g_1g_2g_3} e^{2\pi i(kg_1/G_1+lg_2/G_2+mg_3/G_3)}u_\alpha(g_1g_2g_3/xyz),$$

where $g_1g_2g_3$ are the coordinates of a particular nucleus, $G_1G_2G_3$ the dimensions of the rectangular crystal, and $u_\alpha(g_1g_2g_3/xyz)$ the wave function (as used by Heisenberg) for an electron moving around the nucleus situated at $g_1g_2g_3$. The function with k, l, m represents an electron, in general moving in the direction k, l, m, but pausing at the various atoms on the way. There are as many sets k, l, m allowed as there are atoms in the crystal; for larger k, l, m the function proves to be merely a repetition of one already counted.

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[3] We use here for convenience in writing Pauli's notation u_α, u_β for the spin, rather than the more explicit but more cumbersome notation $u(n/x_i)\ \delta(m_s/m_{si})$ used in a previous paper. See J. C. Slater, Phys. Rev. **34,** 1293 (1929). The method used in the present paper is described, as applied to atoms, in the paper referred to; it should be understood that, although we speak here of using Heisenberg's and Bloch's methods, our actual procedure is quite different from that of these authors.

Now we actually set up the product of functions mentioned in the previous paragraph: we pick one out and let it be a function of the coordinates x_1 of the first electron, a second for the coordinates x_2 of the second, and so on to the nth, and multiply them all together. By the exclusion principle, no function can be chosen more than once. Then we form an antisymmetric combination, by permuting the indices of the electron coordinates, and adding the permuted functions with appropriate signs, obtaining essentially a determinant. These antisymmetric functions are the ones with which we start our perturbation calculation. Many such functions can be set up: there are $2n$ functions of a single electron, of which only n are to be chosen for each antisymmetric function, so that there are $(2n)!/(n!)^2$ different functions. Our perturbation problem is that of finding which linear combinations of these functions most nearly satisfy the wave equation. We may note the restriction of Heisenberg's method as he uses it; he does not include polar states. That is, he does not allow for example the two functions $u_\alpha(a/x)$, $u_\beta(a/x)$ to appear together in any product. This greatly limits the number of functions; but although the terms obtained by it certainly represent the lowest energy levels, since it requires energy to form a positive and a negative ion from two neutral atoms, we do not make this limitation.

Having set up the unperturbed functions, we next make linear combinations of them, by the method described in a previous paragraph. This process can be simplified by using a property of the spin. Every unperturbed function has a certain definite component M_S of spin along the axis, equal to $(n_\alpha - n_\beta)/2$, where n_α is the number of electrons with positive component of spin, n_β the number with negative. If now we neglect the magnetic interaction between the spins and the orbital motion, the problems with each value of M_S can be handled separately: the components $H(i/j)$ from a function with one value to a function with another are zero. The states with a given M_S include, as one readily sees, all those states whose total spin S is equal to or greater than M_S (for just these S's can be so oriented, on the vector model, as to give a component M_S along a fixed axis). Thus by solving each such problem, and comparing, we can identify the spin of each term.[4]

The two methods can be illustrated by the case of H_2. Here there are $4!/(2!)^2=6$ different wave functions. On Heisenberg's method, the four functions for an individual electron can be symbolized by (αa), (βa), (αb), (βb); two of these are to be picked out for each antisymmetric wave function. Thus the six are $(\alpha a)(\alpha b)$; $(\alpha a)(\beta a)$, $(\alpha b)(\beta b)$; $(\alpha a)(\beta b)$, $(\beta a)(\alpha b)$; $(\beta a)(\beta b)$. They are arranged, first, by M_S: the first has the value 1, the next four the value 0, and the last -1. Thus the terms consist of one triplet and three singlets. Among the four terms with $M_S=0$, the first two are polar (and not considered by Heitler and London, or Heisenberg), the last two are non-polar. Immediately one finds that the sum of these non-polar functions is the component of the triplet. We are then left with three functions: the

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[4] This is essentially the method used in the paper already quoted It has already been applied by Bloch to problems in the theory of metals. See F. Bloch, Zeits. f. Physik., **57**, 545 (1929).

two polar ones, and the difference of the non-polar ones, from which to find our three singlets. The difference of the polar ones is antisymmetric in the nuclei, giving one state; their sum, and the difference of the non-polar functions, give two functions symmetrical in the nuclei, between which we finally solve the simple perturbation, resulting now in a quadratic secular equation, and obtain the two remaining singlet states. The energy levels as a function of the distance of separation are plotted in Fig. 1. The energy level of the lowest, ${}^1\Sigma S^N$, is almost exactly as given by Heitler and London, but its wave function contains quite an appreciable contribution from the polar state. The triplet is just the repulsive state of Heitler and London. The other two levels are essentially polar. They go at infinite separation to the energy of $H^+ + H^-$, greater than the other limit by the ionization potential less the electron affinity of H (this rough approximation gives $-\frac{1}{4}Rh$ for the electron affinity, so that the terms go to $5/4Rh$). The lower of these has a minimum; it is presumably the polar part which, by combination with other functions, leads to the experimentally known B state of the molecule. We notice that at large separations the functions behave just like Heisenberg's (extended) unperturbed functions: a triplet and a singlet are non-polar, and go to the lower energy; while two singlets are polar, and go to the higher level.

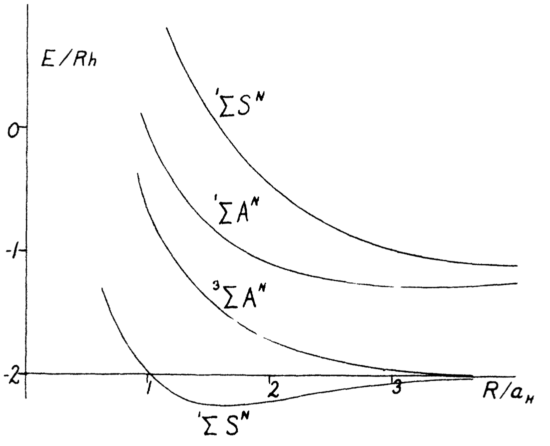

Fig. 1. Energy levels of H_2.

Next we consider Bloch's method for the same problem. His functions for one electron, for this case, are

$$u_\alpha(0/x) = u_\alpha(a/x) + u_\alpha(b/x)$$
$$u_\alpha(1/x) = u_\alpha(a/x) - u_\alpha(b/x),$$

with similar functions for β. (These do not follow quite directly from the general formulas given above; Bloch's functions must be slightly modified for finite systems, for they apply rather to infinite but periodic ones.) The discussion of multiplicity given above goes through without change, if we only substitute 0, 1 for a, b. We can easily show by direct calculation that the resulting unperturbed antisymmetric functions are linear combinations of those found by Heisenberg's method. For example, for $M_S=1$, there is only one function by either method, so these must be identical, except for a numerical factor. By Heisenberg's method the function is

$$u_\alpha(a/x_1)u_\alpha(b/x_2)-u_\alpha(b/x_1)u_\alpha(a/x_2).$$

By Bloch's it is

$$\begin{aligned} &u_\alpha(0/x_1)u_\alpha(1/x_2)-u_\alpha(1/x_1)u_\alpha(0/x_2)\\ &\quad=[u_\alpha(a/x_1)+u_\alpha(b/x_1)][u_\alpha(a/x_2)-u_\alpha(b/x_2)]\\ &\quad\quad-[u_\alpha(a/x_1)-u_\alpha(b/x_1)][u_\alpha(a/x_2)+u_\alpha(b/x_2)]\\ &\quad=-2[u_\alpha(a/x_1)u_\alpha(b/x_2)-u_\alpha(b/x_1)u_\alpha(a/x_2)]. \end{aligned}$$

We can set up the whole perturbation problem in these functions; and the solution can be carried out as easily as before, leading of course to just the same answers. The interesting question now is, how closely do Bloch's individual functions approximate the correct ones, for small values of R? The functions are respectively as follows: a singlet with both electrons in the state 0; a singlet and triplet with one in the state 0, the other in the state 1; and a singlet with both in the state 1. The state 0 corresponds to the lowest vibrational state on Sommerfeld's theory, the state 1 to the next higher one, so that the first state has on the simple interpretation only the zero-point vibrational energy, the next two have each one quantum, and the last two. Examination of the actual wave functions shows that they agree quite closely with the functions of Bloch: the lowest one is made, it is true, by combination of the (00) and (11) states, both being S^N, but the coefficient of the first is about eight times as large as that of the second, when R is such that the energy is at its minimum. The next two are made up of the (01) states. The highest is about eight parts of (11) to one of (00). The energies also show, for high compression, the behavior expected: the two states which should have one quantum of vibrational energy draw together, and the one with two quanta is just about twice as far above the lowest state as those with one. Even the spacing of these levels is just about what would be calculated on Sommerfeld's theory for an electron vibrating in a region the size of the molecule. Thus we see that Bloch's unperturbed functions form fairly good approximations to the real functions for the compressed state, as Heisenberg's do for the extended state.

We can now return to the general case, and make use of the fact that Heisenberg's functions approximate the real wave functions well for large separations, Bloch's for small. First, for the extended system, the energy is the ionization energy, on account of having many ions as well as neutral atoms. For a metal, it requires about 6 volts to form a positive and negative ion from two neutral atoms. Thus if all the atoms were ionized, we should have $n/2$ such pairs, or an energy per atom, or per electron, of about 3 volts. This measures the extension of the group of terms, for large R. It is a simple problem in permutations to find the number of terms of each multiplicity with each energy value in the limit. The one term of highest multiplicity will approach the lowest limit, for large R; it must be entirely nonpolar, for all spins point in the same direction, so that no two electrons can be in the same atom. For the next lower multiplicity, only one electron has a reversed spin; it is the only one which can be in an atom with another electron, so that there can be just one pair of atoms ionized. Following out, we easily see that terms of lower and lower multiplicity, in the limit of large R, lie higher and higher, and at the same time are more and more spread out. They spread in such a way that there are terms of each multiplicity way down to the bottom limit, although not to the top. As we shall see later, for R large but not infinite, in the normal case, the really lowest terms have small spins; but near them are many terms with large spin.

For the compressed system, the arrangement is as given by Bloch's theory. The total extension of the group of terms increases with $1/R^2$; for ordinary values of R, it is of the order of the mean zero-point energy, times n, which is decidedly larger than 3 volts$\times n$. Thus not only do the curves tend upward for decreasing R, giving repulsive energy levels, but they are definitely doing this at the actual size of the metal. The general physical interpretation of this repulsion is obvious: the valence electrons act here approximately as a perfect gas, and the energy levels are those of such a gas as it is compressed adiabatically against gas pressure, the energy varying therefore as $V^{-2/3}$ or as $1/R^2$. Here the terms of high multiplicity lie in the center of the pattern; those of lower spin also average in the center, but are more and more spread out. Since the terms of high spin are so low for large R, but not for small R, they must be even more repulsive than the others. The possibility seems very remote that any terms except those with very low multiplicity could be so low as to have minima, and come into the question for the normal state. We see that for cohesion we are interested only in the very lowest fraction of the whole set of terms. These terms almost all will go to the lowest energy level at infinite separation; they become in this limit non-polar. And the accuracy with which one can compute the lowest states of H_2 from Heitler and London's non-polar functions suggests that here too this may be possible. Accordingly for our actual calculation of these lowest states, we shall use Heisenberg's method with only non-polar functions. We shall find here, as we expect from our qualitative discussion, that the terms of low multiplicity really do lie below, some of them being attractive; while those of high multiplicity are repulsive, the highest spins lying highest. Finally we shall consider the effect of polar terms, and conclude that it is really small on the low energy levels, although not on the wave functions; for it is the polar character of the wave functions which makes conductivity possible.

3. Electric and Magnetic Properties

Conductivity. In the introduction we have mentioned the interpretation of electric conduction on Heisenberg's and on Bloch's scheme. One notices that a single one of Bloch's functions implies conduction—the diagonal term of the momentum matrix is different from zero—whereas with Heisenberg's functions we must have a continual change from one stationary state to another. But it is particularly important to notice that, without polar states, or free electrons, no conduction is possible; we cannot set up combinations of non-polar states with a resultant momentum. For example, with two electrons, we can set up an arbitrary non-polar function $c_1u(a/x_1)u(b/x_2)+c_2u(b/x_1)u(a/x_2)$. If now we compute the momentum, whose operator is $h/2\pi i(\partial/\partial x_1+\partial/\partial x_2)$, the only possibly significant terms are the cross terms, like

$$\begin{aligned}
&c_1c_2\frac{h}{2\pi i}\int u(a/x_1)u(b/x_2)\left(\frac{\partial}{\partial x_1}+\frac{\partial}{\partial x_2}\right)u(b/x_1)u(a/x_2)dv_1dv_2\\
&=c_1c_2\frac{h}{2\pi i}\left\{\int u(b/x_2)u(a/x_2)dv_2\int u(a/x_1)\frac{\partial}{\partial x_1}u(b/x_1)dv_1\right.\\
&\qquad\left.+\int u(a/x_1)u(b/x_1)dv_1\int u(b/x_2)\frac{\partial}{\partial x_2}u(a/x_2)dv_2\right\}.
\end{aligned}$$

On account of the penetration of one atom by the other, the integrals $\int u(b/x_2)u(a/x_2)dv_2$ are not zero. The integral $\int u(a/x_1)(\partial/\partial x_1)u(b/x_1)dv_1$ is also different from zero. But it is exactly cancelled by $\int u(b/x_2)(\partial/\partial x_2)u(a/x_2)dv_2$, as one can show by Green's theorem, so that the whole is zero. On the other hand, if we set up a polar combination like $c_1u(a/x_1)u(a/x_2)+c_2u(b/x_1)u(b/x_2)$, we again get two terms, but now they add, and give a current. As another example, we can take the term of maximum multiplicity in any system. In this term, we have seen by Heisenberg's scheme that each atom has just one electron, so that we expect no conduction. But in Bloch's scheme, each value k, l, m has just one electron. Since each such value is balanced by one with $-k$, $-l$, $-m$, having opposite momentum, the total momentum is zero, and there is again no current.

We can now see the importance of considering exactly the wave functions, as well as the energy levels, of the lowest state. In the ordinary low states there will, of course, be no current. But near the lowest state, if there is to be conductivity, there must be combinations of polar states, having a current, which are assumed in the presence of a field, and whose added energy comes simply from the kinetic energy of the electrons and the self-induction. Such states are possible only on account of the presence of positive and negative ions, with the resulting free and associated electron conductivity.

Magnetism. The lowest state of H_2 is the non-magnetic $^1\Sigma$, and we have found such a situation in general. In the region where the lowest states have their minimum, the metal must surely be in a compressed state, Bloch's arrangement of energy levels must be a good approximation, and the states of large spin must lie very high. We are thus led to the quite general conclusion that the outer electrons, which are largely if not entirely responsible for both cohesion and conduction, cannot produce ferromagnetic effects. If a metal is to be ferromagnetic, there must then be other electrons than these outer ones which are responsible for it, and these others must have smaller orbits, so that at the equilibrium distance of the outermost ones, the inner ones will be relatively further apart, and can be treated as an extended rather than as a compressed system. It is a very attractive hypothesis to suppose that in the iron group the existence of the *3d* and 4*s* electrons provides in this way the two electron groups apparently necessary for ferromagnetism; for it is only in the transition groups that we have two such sets of electrons, and this criterion would go far toward limiting ferromagnetism to the metals actually showing it.

We next ask just how such inner electrons could be ferromagnetic. Certainly the general trend of the terms of high spin to the low energy values at large R is an essential part of the question: there will be terms of large spin near the lowest level. Bloch[5] has discussed the problem, concluding that for large R's the terms of high spin actually lie lower than those of smaller spin (he does not specifically discuss the dependence on R, but his energy formulas all contain it parametrically). This conclusion, however, is not correct; Bloch has merely computed diagonal values of the energy, with respect to his functions, and for large R these by no means form approximations to the actual energy values. From the correct treatment of the problem as we have given it, it is plain that at all R's there are terms of low multiplicity as low as those of high spin, or lower. It may be, however, that the mere presence of so many low terms of high multiplicity may be enough, on account of their high *a priori* probability and large number, to insure that the terms of large spin should be well represented at ordinary temperatures, even though there are low terms of zero spin, and so produce ferromagnetism. If, however, this should prove on calculation not to give the right effect, we should be led to consider Heisenberg's assumption that the normal order of terms is inverted in ferromagnetic atoms, the terms of high multiplicity lying lowest. He has shown by a general argument that electrons of large total quantum number (which the 4*s* electrons of iron have) have an exchange integral of the opposite sign to that found in hydrogen, so that the order of the non-polar terms would be reversed. This we should fit into our scheme in the following way: although this exchange integral is anomalous at large R, it presumably changes sign and becomes normal at smaller R; for first, Heisenberg's general argument only applies at large R; and second, our condition that the energy levels should approach those of Bloch at small R, with the terms of large spin lying high, seems quite general. Thus we should assume that the terms at small R lie as in Fig .1 but that at a considerable value of R, there is a crossing over (in this case the ${}^3\Sigma A^N$ crossing and lying under the ${}^1\Sigma S^N$), described by a change in the sign of the exchange integral K used in the next section from negative to positive. By assuming the existence of an inner group of electrons with these properties, we seem to secure a consistent picture of ferromagnetism. On the other hand, of course it is always possible that ferromagnetism is connected with the fact that the valence electrons of iron have an orbital angular momentum different from zero.

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

4. Cohesion

We are now prepared to begin the actual calculation of the lowest stationary states. We make several simplifications, which we later remove. First, we consider only non-polar states, in Heisenberg's scheme, and disregard exchange integrals except between adjacent atoms; this is the approximation also made by Heisenberg. Finally, for the present, we consider a linear lattice, n atoms uniformly spaced along a line, rather than a space lattice. Our problem, of course, is to compute the matrix of the energy with respect to the wave functions we have chosen, and then solve the problem of making proper linear combinations. The computation of the matrix is simple. By a fundamental formula of the previous paper mentioned above, the diagonal components are a sum, first, of the energies of the separate atoms, which we need not consider; next, a sum over all adjacent pairs, as the pair of atoms a and b, of integrals $J(a/b)$, which is essentially the diagonal energy E_1 of Heitler and London; finally, a sum over all adjacent pairs which have the same spin, of terms—$K(a/b)$, where K is the exchange integral E_2 of Heitler and London. Further, it is easy to show that all non-diagonal terms are zero, except those for which the distributions in the two states differ only by the exchange of an adjacent α and β; in such cases, the term is $-K$. In the normal case, to which we shall refer specifically, J and K as functions of R are both negative, K numerically greater than J. But in Heisenberg's case, K must be taken to be positive for large R, although presumably negative for small R.

To illustrate by H_2, we have one state with both spins parallel; then the energy is $J-K$. Next we have the problems with one parallel, the other anti-parallel; there are two such states (the two polar ones being omitted). Each has the diagonal energy J, and the non-diagonal energy between them is $-K$. Thus the equations for the linear combinations are

$$(J-W)S(1)-KS(2)=0$$
$$-KS(1)+(J-W)S(2)=0,$$

giving energy values $W=J\pm K$, the first evidently being the singlet, the second the component of the triplet.

In the general case, the computation of the matrix is no more difficult; the real problem is the solution of the linear equations for the S's. We cannot do this exactly; but we adopt two methods of approximation, one holding for larger spins, the other for smaller spins. We first discuss the former.

Method for large spins. First we take the problem where all spins are parallel, $n_\alpha=n$, $n_\beta=0$. Here there is but one state. Since with our linear lattice there are $(n-1)$ adjacent pairs, and all spins are parallel, the energy is simply $(n-1)J-(n-1)K$. Since J and K are normally both negative, but K numerically greater than J, this is a positive energy for all values of R, and results in a repulsive term. For Heisenberg's case, on the other hand, K is positive, and this term is attractive. Next we take the problem $n_\alpha=n-1$, $n_\beta=1$. There are now n unperturbed wave functions: the one electron β can be attached to any of the n atoms. We number the functions by the number of the atom where the electron is, only decreased by $\frac{1}{2}$: we have $u_{1/2}\cdots u_{n-1/2}$. Each of these functions will have the diagonal energy $(n-1)J-(n-3)K$, since two of the adjacent pairs now have opposite spins, except for the two functions $u_{1/2}$ and $u_{n-1/2}$ where our β electron is at an end of the lattice, and the energy is $(n-1)J-(n-2)K$. Also, all non-diagonal terms will be zero except those between terms of adjacent number, as for example between those symbolized by

$$\cdots\alpha\,\alpha\,\alpha\,\beta\,\alpha\,\alpha\,\alpha\cdots$$

and

$$\cdots\alpha\,\alpha\,\alpha\,\alpha\,\beta\,\alpha\,\alpha\cdots,$$

and which differ by just one interchange of an α and β. As a result, the perturbation equations will be

$$\begin{aligned}
&[(n-1)J-(n-2)K-W]S\left(\frac{1}{2}\right)-KS\left(\frac{3}{2}\right)=0\\
-KS\left(\frac{1}{2}\right)+&[(n-1)J-(n-3)K-W]S\left(\frac{3}{2}\right)-KS\left(\frac{5}{2}\right)=0\\
-KS\left(\frac{3}{2}\right)+&[(n-1)J-(n-3)K-W]S\left(\frac{5}{2}\right)-KS\left(\frac{7}{2}\right)=0\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-KS\left(n-\frac{3}{2}\right)+&[(n-1)J-(n-2)K-W]S\left(n-\frac{1}{2}\right)=0
\end{aligned}$$

These equations are easily solved; they occur, for example, in the problem of a string weighted at equal intervals,[6] the S's being the displacements of the weights. To solve, we merely assume $S(k)=\overset{\cos}{\sin}(\alpha k)$. The first and last equations give boundary conditions. They become like the others if we introduce an $S(-\frac{1}{2})$ and $S(n+\frac{1}{2})$, the first equation becoming

$$-KS(-\tfrac{1}{2})+[(n-1)J-(n-3)K-W]S(\tfrac{1}{2})-KS(\tfrac{3}{2})=0,$$

and if we further set $S(-\frac{1}{2})=S(\frac{1}{2})$ and $S(n+\frac{1}{2})=S(n-\frac{1}{2})$. These are then the boundary conditions; and to satisfy them we must take

$$S(k/p)=\cos p\pi k/n,\quad \text{where}\quad p=0,1,\cdots,n-1.$$

Now we substitute this form in our difference equations; and we get for W

$$-K\left(\cos\frac{p\pi}{n}(k-1)+\cos\frac{p\pi}{n}(k+1)\right)+[(n-1)J-(n-3)K-W(p)]\cos\frac{p\pi k}{n}=0,$$

from which in each case

$$W(p)=(n-1)J-(n-3)K-2K\cos\frac{p\pi}{n}.$$

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[6] See, for example, Rayleigh's "Theory of Sound."

We now have the transformation coefficients $S(k/p)$ and the energy values $W(p)$ for the rotation of axes to the pth stationary state; the W's are the exact energy levels. They are evidently distributed between the values $W(0)=(n-1)J-(n-1)K$, and $W(n-1)=(n-1)J-(n-3-2\cos\pi(n-1)/n)K=(n-1)J-(n-5)K$, almost, for large n. Obviously $W(0)$ is the energy of the level of highest multiplicity, which we have found before. Thus the levels $1 \cdots (n-1)$ are those of next to highest multiplicity.

Next we take the problem with two electrons of spin β. There are $n(n-1)/2$ such terms: each of the two indistinguishable β's can be on any one of the n atoms, so long as they are not on the same atom. Now it is convenient to denote states by the two atoms, say i and j (each going from $\frac{1}{2}$ to $n-\frac{1}{2}$) on which electrons β are. Our problem becomes analogous to that of a square membrane loaded at equally spaced points. The diagonal terms of the energy are all $(n-1)J-(n-5)K$, unless one of the β's is at an end of the lattice, or unless the two β's are adjacent. There are four non-diagonal terms for transitions from each wave function: for $i \rightarrow i \pm 1$, or for $j \rightarrow j \pm 1$. A typical equation can be written

$$\begin{gathered} -KS(i,j-1) \\ -KS(i-1,j)+[(n-1)J-(n-5)K-W]S(ij)-KS(i+1,j) \\ -KS(i,j+1)=0. \end{gathered}$$

This we satisfy by a product of cosine functions, $S(ij/pq)=\cos(p\pi i/n)\cos(q\pi j/n)$. We easily find that these exactly satisfy the boundary conditions when i or $j=\frac{1}{2}$ or $n-\frac{1}{2}$. There remains the condition when i is nearly equal to j. If $i=j\pm 1$, the diagonal energy is $(n-1)J-(n-3)K$, since the two β's are together; on the other hand, since the β's cannot be on the same atom, the coefficients $S(jj)$ and $S(j+1, j+1)$ vanish, so that only two transitions, rather than four, are possible. If now we define an $S(jj)$ and $S(j+1, j+1)$, we can make the equations of the same form as the general one, if only $S(jj)+S(j+1, j+1)=2S(j+1, j)$. This furnishes our second boundary condition, which is evidently along the diagonal of our square "membrane." Unfortunately we cannot satisfy this condition exactly with our cosine functions; closer investigation shows that one must have much more complicated functions, with hyperbolic cosines, to satisfy it exactly, and one cannot carry the method through for the general case. Approximately, however, we can easily take care of our condition. If the p and q are not too great, so that the "wave-length" of the waves in our membrane is large, we can replace our condition by a differential one: it states that the amplitude at a point next the diagonal is the mean of the two adjacent values on the diagonal, and this very nearly means that the normal derivative of the function, at right angles to the diagonal, is zero. This we can satisfy by making our function symmetrical about the diagonal, or using $\cos(p\pi i/n)\cos(q\pi j/n)+\cos(q\pi i/n)\cos(p\pi j/n)$. We may expect this to hold best for small p and q, not so well for large values. It is clearly not right; for example, it yields $n^2/2$ functions, instead of the correct number $n(n-1)/2$.

Our function is an exact solution of the difference equations, if not of the boundary condition; and we find for the energy

$$W(p,q)=(n-1)J-(n-5)K-2K\left(\cos\frac{p\pi}{n}+\cos\frac{q\pi}{n}\right),$$

where p, q go from 0 to $n-1$, but each pair is counted only once. The term of highest multiplicity comes from $p=q=0$; the $(n-1)$ terms of next highest value are those with either p or $q=0$, but the other not; the remaining terms are of multiplicity smaller by two.

This result can now be generalized without trouble: if we have many β's, the energy levels are given by

$$W=(n-1)J-(n-1-2n_\beta)K-2K\sum_{i=1}^{n_\beta}\cos\frac{p_i\pi}{n}, \quad p_i=0\cdots n-1.$$

The terms where one or more p_i's equal zero are those whose total spin is greater than $(n_\alpha-n_\beta)/2$; those with all p's different from zero are those whose total spin equals $(n_\alpha-n_\beta)/2$. The latter value is evidently enormously greater than the other: every spin has enormously more terms than any higher spin. Thus the terms of a given component of spin along the axis, and those of the same total spin, are approximately the same. We can at once find the distribution in energy of the terms of a given spin. They evidently cluster about the value $(n-1)J-(n-1-2n_\beta)K$; they are distributed about this value like the displacements of a point simultaneously acted on by a sum of n_β periodic vibrations of equal amplitudes but arbitrary phases. This gives, of course, approximately a Gauss distribution. The width of the distribution curve can be derived very easily: we compute the mean square deviation of the energy from its mean, $(W-\overline{W})^2=4K^2[\Sigma\cos(p_i\pi/n)]^2$, the average being taken when each p varies independently from 0 to n. We can take this variation to be continuous rather than discrete. Then the product terms in the square of the sum of cosines all average to zero, the square terms average to $\frac{1}{2}$, and the result is $2K^2n_\beta$. These results may be compared with those obtained by Heisenberg on the group theory, and which as Bloch has shown can also be found from the present method. In the notation of the present paper, putting the number of neighbors of each atom equal to 2, and leaving out the terms in J, Heisenberg finds

$$\overline{W}=-(n-2n_\beta+2n_\beta{}^2/n)K$$
$$\overline{(W-\overline{W})^2}=2K^2n_\beta(1-n_\beta/n)(1+2n_\beta/n-2(n_\beta/n)^2).$$

Our formulas agree with these exact ones to terms in n_β but no further, as we expect from the fact that our approximations hold only for small n_β. For small p's, as we have seen, our results should be good even for large n_β; for the case of ferromagnetism, when on Heisenberg's hypothesis the terms are reversed, these are the lowest terms, so that this result should be very useful here. In the normal case, however, the lowest terms are those of large p, and these are the ones we need for cohesion. About these lowest terms, we can be fairly sure that they lie higher than the lowest ones we have found, or $(n-1)J-(n-1-4n_\beta)K$, since the mean lies higher than the mean we found. For zero spin, for example, we can be fairly sure that the term lies above $(n-1)J+nK$. But this value need not be a very good approximation; we actually find, by the method of the next section, that the lowest term for zero spin is about $(n-1)J+0.290nK$. Fortunately even this has a positive coefficient for K, and is so an attractive rather than a repulsive term.

Method for zero spin. For zero spin, $n_\alpha=n_\beta=n/2$, and there are $n!/(n/2!)^2$ terms. We adopt quite a different method of classifying them. Before, most of the terms of a given n_β had nearly the same diagonal energy; but now the range of energy is large, from $(n-1)J$ for the state with alternating α's and β's so that there are no parallel spins, to $(n-1)J-(n-2)K$ for the state where all the α's come at one end of the lattice, all the β's at the other. With this large range, we find it convenient to classify terms by their diagonal energies; and we find as we should expect, that for the lowest states of the perturbed system we must consider most the low unperturbed states. We do not need to take into account all states: we find that approximately (though by no means exactly) the terms can be divided into a number of non-combining sets, and we set up one such set in the following way. We commence with the lowest state, of energy $(n-1)J$, where α's and β's alternate. Next we consider the $n-1$ states which combine with it, coming from interchanging one pair, and each having the energy $(n-1)J-2K$, except those from the two end pairs, with energy $(n-1)J-K$. We leave these two out, retaining for our set the $n-3$ states which have the energy $(n-1)J-2K$. Each of these has $n-3$ states with which it combines, coming from interchange of one of the $n-3$ adjacent pairs with opposite spins. Of these $n-3$, the two in which the new interchanged pair is next the one already interchanged have the energy $(n-1)J-2K$; the one in which the pair already interchanged is changed back has the energy $(n-1)J$; the two where the end pair is interchanged have the energy $(n-1)J-3K$; and the remaining $n-8$ have the energy $(n-1)J-4K$. We retain for our set only these $n-8$ terms of energy $(n-1)J-4K$. So we proceed, asking which terms combine with those already set up, and retaining just those whose energy is $-2K$ greater than for those with fewer interchanges. We find that a term of our set, with the energy $(n-1)J-2pK$, has non-diagonal terms to p terms of the set of energy $(n-1)J-2(p-1)K$ and to $(n-3-5p)$ terms of the set of energy $(n-1)J-2(p+1)K$. Evidently so long as p is small, the terms we leave out of the set and yet which combine with terms of the set are comparatively few. It is only for the large p's that we make serious error by leaving out these terms, and for large p the diagonal energy is high enough so that for the lowest states of the perturbed system these unperturbed states are unimportant. Thus we may reasonably believe that the low energy levels found by solving this restricted problem will be approximately some of the low levels of the actual problem. We can at least be sure of the following: by the variation principle, they can be no lower than the actual stationary states.

The other sets of non-combining terms which we can set up are easily described, and are of considerable physical interest. Instead of starting from the state with spins alternating, we start from a state where the spins alternate up to a given point; there the sequence is interrupted, and alternation commences again, so to speak, in the opposite phase, as

$$\cdots \alpha\,\beta\,\alpha\,\beta\,\beta\,\alpha\,\beta\,\alpha\,\beta\,\alpha \cdots .$$

With a few such interruptions in the course of the crystal, the energy is very little above the really lowest state; yet a great many individual interchanges would be required to pass to the lowest state. With such a state to start with, we proceed just as we did before, and construct a whole system of states; and the non-diagonal terms between this and the first system come only from high values of p, involving many interchanges, and can be neglected. Physically, at the interruption of phase, one essentially has a slight interruption of crystal structure. Our catalogue of all possible states of the metal includes not only that where it is one perfect crystal, but also where it is composed of many smaller crystals not perfectly joined together. Obviously each problem can be treated separately; physically it would take a very long time to change from one to the other. And obviously each problem will give us essentially the same set of energy levels.

We now take our set of wave functions, and try to solve the perturbation problem between them. For each value of p, we have many wave functions; and we look for those particular solutions for which all these functions have the same coefficient $S(p)$. Afterwards we shall show that we really find the lowest solutions this way. Then, remembering the number of transitions with non-diagonal term K from a given state, computed above, we have for a typical equation

$$-KpS(p-1)+[(n-1)J-2pK-W]S(p)-K(n-3-5p)S(p+1)=0.$$

This set of difference equations for the S's is somewhat similar to what we had before; it also corresponds to a weighted string. But now the properties, and hence the wave-length, change from point to point, and we seek the various overtones. The equation is a close analogue to Schrödinger's equation, in many ways; the fact that it is a difference equation rather than a differential one is quite immaterial. To solve, we assume $S(p)=e^{\int \alpha dp}$, where α is to vary slowly with p. Then $S(p)=e^{\alpha}S(p-1)$, etc., so that we have

$$-Kp+e^{\alpha}[(n-1)J-2pK-W]-e^{2\alpha}K[n-3-5p]=0,$$

$$e^{\alpha}=\frac{-[(n-1)J-2pK-W]\pm([(n-1)J-2pK-W]^2-4K^2p[n-3-5p])^{1/2}}{-2K[n-3-5p]}$$

The equation expresses e^{α} as a function of p, for any particular W. Now we must remember that there are essentially boundary conditions; the S's must remain finite for $p=0$ and $p=$an extreme value. To tell how to apply this condition, we must investigate the solution we have found.

The ratio e^{α} of successive coefficients is real or complex, according as $[(n-1)J-2pK-W]^2$ is greater than or less than $4K^2p[n-3-5p]$. Regarded as a function of p, the limiting cases, where the two are equal, come from $(n-1)J-W=2pK\pm 2K[p(n-3-5p)]^{1/2}$. The right hand side, plotted as a function of p, forms an ellipse; the straight line represented by the left side intersects the ellipse in two points, or in none, depending on the value of W. The region of W where it intersects can be found by computing the maximum and minimum ordinates of the ellipse; that is, the values of $(n-1)J-W$ for which $(d/dp)(2pK\pm 2K[p(n-3-5p)]^{1/2})=0$. This gives $p=(n-3)/10$ $[1\pm(1/6)^{1/2}]=(n-3)\times(0.0592,\ 0.1408)$. At these two limits, substituting, $W=(n-1)J+(n-3)K\times(0.290,\ -0.690)$. For values of W between these limits, there is a range of p for which e^{α} is complex, and the solution is oscillatory; outside this region, which is closed, the solution is in any case exponential. To satisfy our boundary conditions, now, we have a problem much like that with Schrödinger's equation in one dimension; and boundary conditions can be satisfied only if there is an oscillatory region. As a result, the actual energy levels of the problem must lie between the limits given. Closer examination shows that a "quantum condition" can be applied, and that between these limits there are just the number of energy levels there should be. We now have the lowest level: it lies arbitrarily close to our lower limit, or is

$$W=(n-1)J+0.290(n-3)K,$$

as we stated in the last section. In this lowest state, we can show without trouble that the unperturbed wave functions with p near $0.0592(n-3)$ are represented most strongly. Thus the value of p is really quite small; relatively few pairs are interchanged, and we are safely in the region where we can treat the different systems separately.

We have solved our problem for the lowest state in which all terms of the same p have the same coefficient. We can now investigate the effect of removing this assumption, varying the coefficient of one function of a given p in one direction, varying the rest to keep the same total representation for functions of this p, and calculating the change in the energy. When we do this, we find the energy to be a minimum with respect to such variation; in fact, the changes of energy compensate each other to a higher order, showing that the problem is nearly degenerate with respect to these coefficients. Thus we may be rather confident that we have a good approximation to the lowest non-polar states. It is of course obvious that this method becomes worse as we go to higher states.

It is instructive to ask what ordinary perturbation theory would give us for the lowest state. The lowest unperturbed state has the diagonal energy $(n-1)J$; this represents the ordinary first order perturbation calculation. Now we pass to the second order calculation. The lowest state is not degenerate, so that we can use the power series development method. The next term in the expansion is $\Sigma_j(H_{ij}H_{ji})/E_1-E_j)$, summed over all excited states j. Now there are non-diagonal terms H_{1j} only to the $n-1$ states with $p=1$.

Thus the H_{1j}'s are all equal to $-K$, and the energy differences are all given by $E_j=E_1-2K$. Thus we have as second approximation

$$W=(n-1)J+(n-1)\frac{K^2}{2K}=(n-1)J+\frac{1}{2}(n-1)K.$$

This differs from our result in having the factor $\frac{1}{2}$ rather than 0.290; we have only the first term of a series development, but it is reassuring that agreement is as good as it is. For finding the order of magnitude, we could use this term alone; we shall find this simple method useful with the space lattice.

Effect of polar states. One can make an estimate, by a method like that used here, of the effect of the polar states in depressing the non-polar ones, which alone we have considered so far. We can build up a series of states by starting with a given non-polar state; then removing one of the electrons to an adjacent atom, producing a positive and a negative ion; then removing a second; and so on. The series of states so found behave formally like those used above. If we solve the problem by the previous method, or by the second order perturbation method, we get a further depression of the lowest state, which again can be written as

$$(n-1)\times\sum\frac{\text{square of non-diagonal term}}{\text{energy difference}}$$

The non-diagonal term which comes in here is presumably of the same order of magnitude as before, although it is a somewhat different integral. But the diagonal energy difference is now essentially an ionization energy, which is of the order of several volts, rather than the fraction of a volt that K is. Thus the effect on the energy is a number of times smaller than what we found before, and we can neglect it. It is not worth while calculating more accurately, in this approximation; for with H_2, it appears that on account of the lack of orthogonality of the wave functions, the actual depression of the energy is very much less than this rough method would indicate, although the effect on the wave function is about what we should expect. One can reasonably believe for this reason that the polar states in the crystal depress the energy only very little. But we recall that their effect on the wave function is to introduce free electrons. By our rough method described above, we infer that the fraction of free electrons is of the order of 1 percent, for reasonable choice of the constants. This could easily be in error by a factor of 10 either way; but at least we see that a definite meaning can be attached to the number of free electrons, and that there is a definite procedure for calculating this number.

Normalization and orthogonality. We have not considered the lack of orthogonality of the wave functions, resulting in factors like the $1/1\pm S$ of Heitler and London. When one tries to do this, one immediately strikes a difficulty which appears insurmountable: the factor in the denominator, instead of being like $1+S$, is like $1+nS+\cdots$, where n is the number of atoms, so that the term nS is enormous compared with unity. On examination of simple cases, it appears that the remaining terms, coming from other permutations than the simple interchange, are also important, in many cases the terms almost cancelling each other. Further, in every expression for energy, like the simple $(J \pm K)/(1 \pm S)$, there are more terms in the numerator, also of great importance. But the simple cases give no suggestion of how to treat the general case. The key to this difficulty comes from Bloch's method. For example, the term of maximum multiplicity has one function, which can be expressed either by Heisenberg's or Bloch's functions. But the difference is that Bloch's functions are really orthogonal, unlike Heisenberg's, so that we meet no such difficulty. Of course, the same terms occur, but now in the normalization of the individual functions. And the numerators, and denominators like $1 + nS + \cdots$, appear as products of n factors, each of approximately a simple Heitler and London form; further, all but one or two of these factors of the denominator cancel against equal factors in the numerator, giving very simple results. Essentially the same method can be used with the other states; for this method is one for treating a determinant of Heisenberg's wave functions, and converting it into a determinant of Bloch's functions; and all of our wave functions are products of two such determinants. When we calculate in our case, it appears that the terms S will have small effect; we are roughly half way between the cases $1 + S$ and $1 - S$, and the effects of S nearly average out. This method at the same time gives the proper way of considering more distant pairs, as well as adjacent ones; these contribute the further terms in the numerators, as $J \pm K + \cdots$. We see from the next paragraph that these more distant pairs are really quite important.

Method for space lattice. So far, we have spoken about a linear lattice of atoms, rather than a space distribution. We now extend this theory to a crystal; but we shall not carry it through in the same detail. We consider only the problem of zero spin, and use our second order perturbation approximation. Let us take the body-centered cubic lattice, which the alkalies have. The lowest unperturbed state of this lattice can be set up much as with the linear one: we let the electrons at the corners of the cubes have the spin α, those at the centers the spin β. Then each electron is surrounded by eight others of opposite spin, so that if we consider only adjacent pairs, the diagonal energy of this state is $4nJ$, where there are n electrons, $4n$ pairs. This lowest state now has non-diagonal terms, each equal to $-K$, to the $4n$ states obtained by interchanging an adjacent pair. Each of these states has two misplaced spins, each surrounded by 7 spins of the same sign, so that the energy has a term $-14K$. Thus for our perturbation problem, we have a non-diagonal energy $-K$, an energy difference $14K$, and $4n$ non-diagonal terms, so that the perturbed energy is $4nJ + (4nK^2/14K) = 4nJ + (2/7)nK$.

This formula is rather significant. We compare the energy with that of the lowest state of the diatomic molecule, $n = 2$, which is $(n/2)J + \frac{1}{2}nK$. We observe that for the crystal the coulomb interaction, the term J, has a coefficient eight times as great: each atom has eight neighbors instead of one, each penetrating. On the other hand, the valence term K has a coefficient only 2/7, instead of 1/2. The valence, so to speak, is spread out among all the neighbors, and weakened in the process. It is partly on this account that we can say that the coulomb interaction is the more important part of the cohesive force, in metals.

We have considered only those pairs with smallest separation, and they give a definite attraction. But in this lattice, there are not only the eight nearest atoms at distance R; there are also six, in directions parallel to the edges of the cube, at distance of $1.155R$, and these have parallel spins, producing therefore a repulsion. In the diagonal energy, each pair will then contribute an energy $J-K$, a positive amount, so that the diagonal energy of the lowest state if $4nJ+3n(J(1.155\ R)-K(1.155\ R))$. The next higher diagonal energy also will differ from this not merely by $-14\ K(R)$, but also by an amount $12\ K(1.155\ R)$, because by interchange of two spins some of these repulsive terms are removed. Thus the lowest energy level, counting also these pairs, is

$$4NJ(R)+3n(J(1.155R)-K(1.155R))+\frac{4nK^2(R)}{14K(R)-12K(1.155R)}\cdot$$

This results, on computation, in a much weakened attraction. If we were to consider in succession the effects of pairs at greater and greater distance, we should come in succession to attracting atoms with antiparallel spin, and repulsive ones with parallel, so that the successive approximations to the energy would oscillate, falling first above, then below, the true value.

Application to sodium. For the sodium crystal, approximate calculations have been carried out, to test these formulas. These were made by taking a simple analytical expression for the wave function of the valence electron of sodium, and computing the integrals J and K. The details of the calculation will not be given here. The first thing that one notices is that, for Na, J is several times larger in proportion to K than in hydrogen. It is this fact, taken together with the increased coefficient of the J term, that results in the importance of the coulomb term. It is also significant in connection with the question, why do the alkalies, and metals in general, form metallic lattices, while hydrogen does not? We can see the essential answer from our energy formulas of the previous page. For substances where J is the important term, the coefficient of J will be greater, and the energy lower, for the crystal than for the same number of atoms in diatomic molecules, and the crystal will be the stable form. For hydrogen, on the other hand, the valence term K is the important one. Here the coefficient in the molecular form is greater; and even if the metallic form of such a substance were stable in the sense of having a minimum of energy for some definite size, as seems quite possible, still the energy in the molecular state would be lower. The atoms in the crystal would tend to form pairs, resulting in a molecular lattice; the molecules would repel each other, and would be held together only by van der Waals forces, which have been neglected in this paper. This seems to be exactly what hydrogen does.

The numerical values for Na are approximately as follows. If we take only the adjacent pairs, the minimum comes at $R=4.9a_H$ approximately, rather seriously less than the correct value 7; this can partly be explained by the observation that the best atomic wave function for use in the crystal would be more extended than that determined from the free atoms, which are here used. The energy at this point comes out about -40 kg cal/gm mol, the coulomb term supplying about four fifths of this; the observed heat of vaporization is 26.4 kg cal, so that this gives, as we should expect, too large a value. If now we consider the repulsive pairs at distance of $1.155\ R$, the situation is quite changed. In the first place, the energy is reduced from -40 to about -9 kg cal. When we remember that these two values are the first two terms of a series, whose value oscillates on both sides of the answer, it seems very reasonable that the final result should be not far below the experimental value. The problem of properly computing this energy must be done by the method, using Bloch's functions, described in the preceding section. In the next place, the minimum of the curve is greatly broadened: for quite a range of values, from $R=4.9$ (the previous minimum) to $R=7$, the energy stays about constant, the change of the attractive term being just about balanced by the relatively more rapid change of the smaller repulsive effect. (For smaller R's, a situation can be found when the denominator $14\ K(R)-12\ K(1.155\ R)=0$, so that the function becomes infinite; but this is without physical significance.) No doubt a persistence of this effect in the final answer helps to correct the improperly low grating space we have already found. It also is interesting in connection with the compressibility. The alkalies are remarkably compressible, and if we compute the compressibility for the case where only adjacent pairs are considered, the result is too small by a factor of 2 or 3. On the other hand, considering the next set of atoms, our very broad maximum would give much too great a compressibility. Here again it seems that our result may oscillate, perhaps approaching eventually something near the right value.