REVIEWS OF MODERN PHYSICS VOLUME 25, NUMBER 1 JANUARY, 1953

Ferromagnetism and the Band Theory

J. C. Slater

Massachusetts Institute of Technology, Cambridge, Massachusetts

Two rival methods of handling molecular problems, the Heitler-London and the molecular orbital methods, have been used for many years, and they have their counterparts in magnetism in the Heisenberg and the energy-band methods. The first part of this paper shows that the Heitler-London and Heisenberg methods, as usually applied, are not appropriate for problems containing more than a few electrons. The reason is the lack of orthogonality of the one-electron orbitals of atomic type. This involves the presence of overlap integrals which, if included in the calculation, make the method essentially divergent and unsuitable for numerical calculation if the product of the number of electrons in the system, times an overlap integral between nearest neighbors, is large compared to unity, which in practice confines the application to problems of a few electrons. Most applications of the method, including all applications of the Heisenberg method to ferromagnetism and antiferromagnetism, disregard many integrals which are not as a matter of fact negligible, and for this reason cannot be regarded as valid.

Van Vleck many years ago tried to overcome this difficulty, but his results are only partially satisfactory on account of lack of generality. The straightforward way to overcome it is to use really orthogonal one-electron orbitals, either molecular orbitals or Wannier functions, and the remainder of the paper considers how the familiar facts of ferromagnetism are to be explained on this basis. If we use a single determinantal wave function composed of energy-band orbitals, we have the familiar energy-band or collective electron theory of ferromagnetism. This simple method may well be fairly accurate at small internuclear distances; it predicts correctly that ferromagnetism must be impossible when the atoms are close enough together to broaden the energy bands greatly. For large internuclear distances, however, it leads to quite wrong limiting behavior, since it gives a wave function involving a considerable contribution of ionic states. To eliminate these ionic states, at large internuclear distances, we must make linear combinations of different determinantal functions, corresponding to different assignments of electrons to orbitals. The results of such a calculation are sketched.

To treat magnetic problems properly, we must make such calculations for different total spins, calculate the energy of the states of different magnetizations as a function of internuclear distance, and see which states lie lower, the magnetic or nonmagnetic. At infinite separation, the energy will be independent of total magnetization, since in this limit the spins of different atoms can be oriented in any arbitrary way without affecting the energy. At very small distances, the elementary band theory shows that the nonmagnetic state must lie below the magnetized state, so that ferromagnetism is impossible. At intermediate distances, the elementary theory can show only that ferromagnetism is possible, not that it is necessary; to find whether it actually exists, we should really have to carry out a calculation of the type described. If we find ferromagnetism, we shall necessarily find that the energy difference between nonferromagnetic and ferromagnetic states was zero at infinite internuclear distance, increased as the internuclear distance decreased, went through a maximum, and then went to zero and changed sign. This behavior is often postulated for the Heisenberg exchange integral, although we do not feel that this integral has the direct theoretical meaning often ascribed to it.

These problems are closely related to the correlation energy, which is discussed. We do not feel that the familiar Wigner-Seitz calculation of correlation energy is very accurate; the correlation energy is in fact a function of magnetization, decreasing numerically with decreasing internuclear distance, and its interpretation cannot be given properly except by considering its intimate connection with magnetization. The net result of the present discussion is that to give a proper account of ferromagnetism, we are forced to use orthogonal orbitals and, therefore, must make close connection with the band theory. We must, however, carry our theory further than has usually been done, though the prediction of the elementary band theory, i.e., that ferromagnetism is impossible for broad bands and can exist only for narrow bands and electronic wave functions which overlap only slightly, is verified by the present more accurate approach.

As an illustration of the general method of calculating magnetic energies described in this paper, we may mention the recent calculation of Meckler, not yet published, on the oxygen molecule. This has been carried out by setting up many determinantal wave functions formed from orthogonal atomic orbitals made out of the original nonorthogonal orbitals. The secular equations involving these determinantal functions were solved by use of a digital computer. The resulting energy levels and wave functions reduce to the proper type to represent the ^3P ground state of the oxygen atom at infinite internuclear distance. Meckler's energy for the triplet ground state is very accurate; that for the next singlet excited state is quite good. The energy separation between singlet and triplet shows the behavior expected for the energy difference between a ferromagnetic and nonferromagnetic state, being zero at infinite distance, then increasing, going to a maximum, then decreasing again. As far as the writer is aware, this is the first time when such a behavior has been found as a result of straightforward calculation from quantum mechanics.

FOR many years, there have been two competing approaches to problems in molecules and solids. First there is the Heitler-London method for molecules, with the related Heisenberg method for magnetism; second, there is the molecular orbital method for molecules, with the energy-band method for solids. Many students of molecular structure, following Pauling, have based their work on the Heitler-London method, and many students of magnetism, following Van Vleck, have used the Heisenberg theory as fundamental. Another school of molecular theory, following Lennard-Jones and Mulliken, has used the molecular orbital method; and other workers in magnetism, as for instance Stoner, have used the energy-band or collective electron method. It has often been shown that for simple systems, in particular the hydrogen molecule, the two methods as properly amplified are equivalent, and this has been regarded as a justification for the use of either method for complicated molecules and solids. For a very long time the present writer has believed otherwise: He believes that the Heitler-London and Heisenberg methods are by their nature incapable of being rigorously applied to systems containing more than a very few electrons, except in special cases like ionic crystals, and feels, therefore, that they are unsuited for most problems in the structure of molecules and solids and for almost all problems in magnetism. It is the purpose of the present paper to give the reasons for this belief and then to outline how the energy-band method can be adapted to problems of solids, particularly in the limit of large internuclear distance where difficulties in its application are sometimes pointed out.

I. THE OBJECTIONS TO THE HEITLER-LONDON AND HEISENBERG METHODS

All methods under discussion work with one-electron orbitals; the characteristic of the Heitler-London and Heisenberg methods to which we object is that in these methods the orbitals represent atomic functions on different atoms, and hence necessarily are not orthogonal to each other. In the present section we shall make two points: first, that for systems of more than a few electrons, the use of nonorthogonal orbitals involves us in practically insuperable computational difficulties; secondly, that the use of nonorthogonal orbitals is inherent in the Heitler-London and Heisenberg methods. Before making these points we must note that there are three general methods which have been proposed for using one-electron orbitals for many-electron problems. Before 1929, the group theory was generally used. This method involved a great deal of superfluous mathematical machinery, and it was supplanted in 1929 by the determinantal method suggested by the present writer[1] and by the spin operator method proposed by Dirac.[2] The determinantal method is completely general and will be made the basis of the discussion of the present section. The spin operator method, which has been widely used by Van Vleck[3] and his school for magnetic problems, is less general. It will be shown in Sec. II that this lack of generality makes it inadequate as a foundation for a theory of magnetism.

We now take up our first point: that the use of nonorthogonal orbitals involves practically insuperable difficulties in many-electron problems. The writer[4] has discussed in principle the application of the Heitler-London method, using nonorthogonal orbitals, to such problems and has carried through illustrative cases involving a small number of electrons. The characteristic step in this application is the calculation of matrix components of the energy of the n-electron system, and of unity, between determinantal n-electron functions formed from nonorthogonal one-electron orbitals $u_1(x)$, $u_2(x)$, etc., where the orbitals, and the coordinates, x, involve both spacial coordinates and spin. Once these matrix components are calculated, we can set up a secular equation for finding the energy levels, and the combinations of determinantal functions which best represent the correct wave function. The difficulties arise in the calculation of these matrix components, and can be illustrated by the very simplest example, the calculation of the diagonal component of the matrix of unity with respect to a determinantal function $\det|u_i(x_j)|$, which is required in order to normalize the determinant, provided the u_i's are normalized but not orthogonal. We wish in other words to compute $\int \det|u_i^*(x_j)|\det|u_i(x_j)|dx_1\cdots dx_n$. We can at once reduce this to the form

$$n!\sum(\text{permutations } P)\int u_1^*(x_1)\cdot u_n^*(x_n)(\pm P)u_1(x_1)\cdot u_n(x_n)dx_1\cdots dx_n, \quad (1)$$

where P represents a permutation of the subscripts of the u's. The term of this summation for which P represents the identity is unity, by the normalization of the u's; and if the u's were orthogonal, all other terms would give zero, so that the result would be simply $n!$, and the normalized determinant would be $(n!)^{-\frac{1}{2}}\times\det|u_i(x_j)|$. If the u's are not orthogonal, however, we shall next have $n(n-1)/2$ terms involving single interchanges of two subscripts. If the kth and lth are interchanged, the integral in (1) will be

$$-\int u_k^*(x_k)u_l^*(x_l)u_l(x_k)u_k(x_l)dx_k dx_l = -\left[\int u_k^*(x_k)u_l(x_k)dx_k\right]^2, \quad (2)$$

the square of the overlap integral between the kth and lth atomic orbitals. We know that these integrals fall off rapidly with internuclear distance, so that only those terms of (1), involving interchange of two subscripts, will be appreciable in which k and l represent near neighbors. There will be of the order of magnitude of $zn/2$ pairs of near neighbors in the system, if z is the number of near neighbors which a given atomic orbital has. Thus, from interchange of pairs of subscripts we shall have of the order of $zn/2$ terms in the summation (1), each of the order of magnitude of the square of the overlap integral between neighboring atoms. Since these squares can well be of the order of 0.01 or larger in practical cases, it is clear that the sum of the terms of (1) coming from simple interchange can be of the order of n, as compared to unity for the leading term. Similarly, by considering more complicated permutations we see that next we have sets of terms adding to something of the order of n^2, then something of the order of n^3, and so on. If n is more than a very small integer, it is clear that this sum involves terms each of which

---

[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[2] P. A. M. Dirac, Proc. Roy. Soc. (London) **A123**, 714 (1929); or *The Principles of Quantum Mechanics* (Oxford University Press, London, 1947), third edition, Chap. IX.

[3] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932); Phys. Rev. **45**, 405 (1934); J. H. Van Vleck and A. Sherman, Revs. Modern Phys. **7**, 167 (1935); J. H. Van Vleck, Physica **15**, 197 (1949); J. phys. et radium **12**, 262 (1951); P. W. Anderson, Phys. Rev. **79**, 350, 705 (1950); and many other references by Van Vleck and students.

[4] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

is enormously larger than the preceding one. Closer examination shows that the signs of the terms alternate, so that the sum can be finite; but it will be found as the difference of very large positive and negative quantities and, hence, is entirely unsuited for computation. We shall point out later how to get around this difficulty, but the present point is that it cannot be avoided by direct and straightforward methods.

Closely related to the difficulty just mentioned is that encountered when we start calculating the matrix components of the energy and the exchange integrals which are involved in the calculation. The energy operator H is a sum of quantities $f_1\cdots f_n$, each involving the coordinates of one electron only (the kinetic energy operator, plus the potential energy in the field of all the nuclei), and of quantities g_{ij}, the Coulomb repulsive energy between the ith and jth electrons. The resulting integral is just like (1), but with the operator H inserted after the factor $u_n^*(x_n)$. The integral coming from the identity permutation is the Coulomb integral, which will not concern us further; it is easy to compute. The only remaining term in the two-particle case is the ordinary Heitler-London or Heisenberg exchange integral,

$$J_{12}=\int u_1^*(x_1)u_2^*(x_2)(f_1+f_2+g_{12})\,u_2(x_1)u_1(x_2)dx_1dx_2. \quad (3)$$

In the general case of n particles, if the u's are orthogonal, two things happen. First, the exchange integral (3) reduces to the form

$$J_{12}=\int u_1^*(x_1)u_2^*(x_2)g_{12}u_2(x_1)u_1(x_2)dx_1dx_2. \quad (4)$$

Second, the sum in the expression similar to (1) reduces to the Coulomb term, minus the sum of the exchange integrals, of form (4), for all pairs of orbitals. If the u's are not orthogonal, however, there is no comparable simplification. We have a very great variety of types of exchange integrals, involving permutations of many electrons, which by no means vanish. The whole problem of computing the diagonal or nondiagonal matrix component of energy between two determinantal functions becomes even more formidable than that of computing the normalization integrals.

Thus, we see the computational difficulties involved in the use of nonorthogonal orbitals. Unless some simplification can be made, they are quite insuperable for anything but very simple problems, and no one has tried to carry through all the terms in a complicated case. Much work has been done, in both molecular and magnetic problems, by making the following assumptions: We assume that the diagonal matrix component of energy can be written as the Coulomb integral, minus the sum of the J_{kl}'s, as we should have for orthogonal u's, but use the form of J_{kl} given in (3), appropriate only for nonorthogonal u's: and we disregard all overlap integrals in the matrix component of unity. These assumptions are completely unjustified. The molecular orbital or energy-band methods can be used to make accurate calculations of molecular energy levels, as Mulliken and Lennard-Jones and Coulson and others of their school[5] have shown; and the energy-band method can be used for accurate calculations of the structure of solids, as Löwdin[6] and others have shown. These calculations, though made with a different starting point, eventually encounter the same exchange and overlap integrals which are met in the Heitler-London and Heisenberg methods. It is very clear from these accurate calculations that the terms which are disregarded in the approximate methods described above are by no means negligible, and that if they are omitted from a correct calculation, agreement with experiment is completely vitiated.

We reject completely, then, that large body of work which has simply neglected the nonorthogonality or overlap of one-electron orbitals, as representing an unjustified oversimplification which forms no valid approximation to the real predictions of wave mechanics. To be taken more seriously, however, is Van Vleck's[7] attempt to justify the procedure outlined in the paragraph above. This attempt was made as an answer to the criticism of Inglis[8] regarding the catastrophe produced by nonorthogonality in a many-electron system. This criticism was equivalent to that made in the preceding paragraphs of this section; the same difficulty had been pointed out earlier by the present writer.[9] Van Vleck showed essentially that the matrix components of unity and of energy between two determinantal functions, which we have been considering above, could be factored, if we neglect certain terms. The final answer in every case will be a ratio of two integrals, one coming from the energy in the numerator and one from the matrix of unity in the denominator. Most factors in numerator and denominator are identical and can be canceled. The remaining ratio then proves, as Van Vleck showed, to be of the sort described in the preceding paragraph, and to involve sums in which the number of integrals coming from simple exchange was only proportional to z, the number of near neighbors, rather than to $nz/2$.

If Van Vleck's treatment had been really general, it would have provided the complete answer to the difficulties. Unfortunately, it was not; we have mentioned that certain terms had to be omitted, and the

---

[5] R. S. Mulliken and R. G. Parr, J. Chem. Phys. **19**, 1271 (1951), and many other references given there; numerous papers in Proc. Roy. Soc. (London) **A207**, 1–136 (1951), and many references given there.

[6] P.-O. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals*, thesis, Uppsala, 1948; J. Chem. Phys. **18**, 365 (1950); **19**, 1570, 1579 (1951).

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

[8] D. R. Inglis, Phys. Rev. **46**, 135 (1934).

[9] J. C. Slater, Phys. Rev. **35**, 509 (1930); see particularly pp. 526–527.

results were worked out only for special cases. We can give an idea of how it works, however, from our simple example of the normalization integral $\int \det|u_i^*(x_j)| \times \det|u_i(x_j)|dx_1\cdots dx_n$. At the same time our example will show how Van Vleck's method can be extended so as to be perfectly general. Suppose we have a particularly simple case, in which the n functions u_i represent atomic functions, all corresponding to electrons of the same spin, on the n lattice sites of a regular lattice. In other words, our determinantal function represents a state in which we have a completely filled set of wave functions, one per atom, corresponding to one spin. Then we know that we can make from the u's a set of n normalized, orthogonal Block functions, which can easily be shown to be

$$b_i(r)=d_i n^{-\frac{1}{2}}\sum(\mu)\exp(ik_i\cdot R_\mu)u(r-R_\mu), \tag{5}$$

where

$$d_i=\left\{\sum(R_m)\exp(ik_i\cdot R_m)\int u^*(r)u(r-R_m)dv\right\}^{-\frac{1}{2}}. \tag{6}$$

Here r is the vector position of an electron, and $u(r-R_\mu)$ is an atomic function located on the lattice point at R_μ and corresponding to a + spin. If the u's on different lattice sites were orthogonal, the quantity d_i would be unity; if they are not orthogonal, we have an additional term which involves only a summation over the z near neighbors of an atom. There are n functions $b_i(r)$, corresponding to the n values of the propagation vector k_i consistent with the boundary conditions in the crystal (for instance, periodic boundary conditions). Now we know that if we form the determinant $(n!)^{-\frac{1}{2}} \times\det|b_i(r_j)|$, this function will be normalized, since the b's are normalized and orthogonal. However, we also know by general properties of determinants that this determinant is proportional to $(n!)^{-\frac{1}{2}}\det|u_i(x_j)|$. In fact, it is not hard to find the relation between these two determinants and to show that the function $(n!)^{-\frac{1}{2}}\{\Pi(i)d_i\}^{\frac{1}{2}}\det|u_i(x_j)|$ is normalized. In other words we have found our difficult normalization integral, for this special case, and we have shown that it factors into a product of d_i's. This is the simplest example of the factoring procedure that Van Vleck used in the reference quoted above, although he did not use the Bloch functions directly. It is clear that the product of all the d_i's, as defined in (6), will have the form described earlier: It will have unity for the leading term, then something like zn terms each of the order of an overlap integral between neighboring atoms, then $(zn)^2$ terms involving products of overlap integrals, and so on. But its factorization has simplified the situation. We can carry out a similar factorization in the energy integral, and the ratio of the two, giving the diagonal energy of this state, has most of the factors canceling in numerator and denominator, reducing to a simple final result, in accordance with the findings of Van Vleck.

We thus see how Van Vleck's result can come about: that the catastrophe of nonorthogonality in a many-electron system really follows from the method of calculation, and is not inherent in the problem. We may well believe that if we could really set up a Heitler-London approximation for a problem of many electrons, and carry through the calculations exactly, the results would be quite reasonable and might well form as good an approximation as with hydrogen. Nevertheless, the computational difficulties remain. We may ask, then, can we not extend Van Vleck's method to the general case, without making the approximations which he was forced to make in reference 7? The answer is obvious from the discussion we have just given: We can rewrite our problem in terms of really orthogonal one-electron orbitals, and then everything goes through simply. We have just pointed out that we can use Bloch combinations of atomic orbitals, so as to get orthogonal functions; this was pointed out in reference 9. We can also use Wannier functions,[10] orthogonalized one-electron orbitals, as the writer has done for magnetic problems,[11] and as Löwdin[6] has done for problems in cohesive energy in crystals. Either of these methods gets away from the nonorthogonality catastrophe; and it is doubtful whether any essentially independent method would accomplish the same purpose.

By introducing orthogonal orbitals, either of the Bloch or the Wannier type, then, we escape the nonorthogonality difficulty. But at the same time we find that we no longer have the Heitler-London method; we have instead the energy-band method, which is the one which the writer is advocating. We might think that all we had to do was to introduce orthogonal orbitals, and then proceed exactly according to the pattern of the Heitler-London and Heisenberg methods; but this is not true, and those methods depend essentially on the use of nonorthogonal orbitals. Thus, we come the second principal point of the present section, the fact that nonorthogonal orbitals are essential to the Heitler-London and Heisenberg methods. The writer has already pointed this out[12] with reference to problems in molecular structure. Let us state the argument in somewhat different language, appropriate for the magnetic problem. Let us suppose specifically that we set up Wannier functions, which in many ways resemble atomic functions, and that we set up a theory analogous to the Heisenberg theory of ferromagnetism, using these functions. They are orthogonal, and hence the exchange integrals J_{kl} take the form (4), which is necessarily positive, since it represents the electrostatic interaction of a charge distribution with itself. But we remember that a positive exchange integral, in Heisenberg's theory, corresponds to ferromagnetism. We should therefore conclude, if we used the Heisenberg method naively, that all substances were ferromagnetic, an obviously absurd conclusion. To get a negative exchange integral, as in the Heitler-London method, we

---

[10] G. Wannier, Phys. Rev. **52**, 191 (1937).

[11] J. C. Slater, Phys. Rev. **52**, 198 (1937).

[12] J. C. Slater, J. Chem. Phys. **19**, 220 (1951).

must have the interaction term between electrons and nuclei in f_1 and f_2 in the expression (3); these are the only negative terms in the exchange integral, and in the case of the hydrogen molecule they outweigh the positive terms. But they are missing with orthogonal orbitals. Since most substances are not ferromagnetic, it is clear that we must carry a calculation, starting with Wannier functions, through a further step than we are used to in the Heitler-London or Heisenberg methods, to get results of any reliability.

We can easily see what this additional step is, by considering the familiar case of the hydrogen molecule. If a and b represent (nonorthogonal) atomic functions on atoms a and b, we can set up orthogonalized atomic orbitals, as in reference 12, by the relations $A=c_1a+c_2b$, $B=c_2a+c_1b$, where c_1 and c_2 are determined to make A and B orthogonal and normalized. We can set up the spin degeneracy problem corresponding to one electron being in orbital A, one in B, either electron having either spin. The resulting spin degeneracy problem is carried through exactly as in the Heitler-London calculations for H_2, and it results in a singlet and a triplet. The orbital part of the triplet wave function (disregarding normalization) is $A(1)B(2)-B(1)A(2)$, where 1, 2 symbolize the electronic coordinates; substitution shows that this is the same as $a(1)b(2)-b(1)a(2)$, so that this method gives the same result for the triplet as the Heitler-London method, and hence the energy of this state must be the same. For the singlet, the wave function is $A(1)B(2)+B(1)A(2)$. This singlet state must lie above the triplet since as we have seen the exchange integral is always a positive for orthogonal wave functions. Thus, the singlet state as given by this method is not attractive; this fact was pointed out in reference 12, but this is a more direct proof than is given in that reference. Since we know that the Heitler-London singlet state lies below the triplet, and has an energy low enough to lead to the molecular binding in H_2, it is clear that the wave function for the singlet given by the orthogonal atomic orbitals is very incorrect. Let us see why this is true, by writing A and B in terms of a and b. When we do this, we find the wave function to be equivalent to

$$(c_1^2+c_2^2)[a(1)b(2)+b(1)a(2)]+2c_1c_2[a(1)a(2)+b(1)b(2)]. \quad (7)$$

The first term is the ordinary Heitler-London function for the singlet, which gives an energy below the triplet; but the second is the Heitler-London function for the ionic state where both electrons are on the same atom. Since this state has a much higher energy, it is the admixture of this ionic state which spoils the singlet wave function as calculated by the Wannier function method.

We know, of course, that the Heitler-London calculation for H_2 is surprisingly good, so that to get a good wave function for the singlet state, we must modify (7) to restore it very nearly to the Heitler-London form $a(1)b(2)+b(1)a(2)$. To do this, starting with the Wannier functions, we must consider a configurational interaction between the state already described, in which one electron is in a state A, one in state B, and the state where both electrons are in orbital A, or both in B. The singlet function of proper symmetry which can be formed from this configuration is $A(1)A(2)+B(1)B(2)$. Writing this in terms of a and b, it is

$$(c_1^2+c_2^2)[a(1)a(2)+b(1)b(2)]+2c_1c_2[a(1)b(2)+b(1)a(2)]. \quad (8)$$

The result of a configurational interaction between this wave function and that given in (7) will yield two final functions, one of which will be close to the function $a(1)b(2)+b(1)a(2)$, or the Heitler-London ground state, the other close to the Heitler-London ionic function $a(1)a(2)+b(1)b(2)$. In other words, the use of Wannier functions artificially introduces an ionic character into the wave functions, and a configurational interaction with the configuration in which a Wannier function is occupied by two electrons, one of each spin, is absolutely necessary in order to counteract this ionic effect and get a description of covalent binding, or of a negative Heisenberg exchange integral or a nonferromagnetic state. It is the absolute necessity of this configurational interaction which distinguishes this calculation from the ordinary Heitler-London or Heisenberg approach, where the interaction with ionic configurations is regarded as a refinement, which is generally disregarded.

The net result of this section, then, is that a direct calculation of any molecular problem except the very simplest by the Heitler-London method is impossible. If the calculation could be made, the answer might be quite a good representation of the true wave function. The only practical way to get at it, however, is to start with orthogonal orbitals, either of the energy-band Bloch type or of the localized Wannier type. When we do this, the calculation becomes practicable. But all exchange integrals become positive, which puts us on our guard against using a naive form of the Heitler-London or Heisenberg method. Rather, to get correct results, it is essential to consider configuration interaction with ionic states, in which one Wannier function is occupied by two electrons. When this is done, the method may be expected to give good results; but it is now so far from the original Heitler-London or Heisenberg method that it should no longer be described in terms of those methods.

II. OBJECTIONS TO THE DIRAC SPIN OPERATOR FOR MAGNETIC PRABLEMS

Before we go on to the applications of the energy-band method, we should consider one additional point, the validity of the expression

$$-\tfrac{1}{2}\sum(\text{pairs } k, l)J_{kl}(1+4s_k\cdot s_l), \quad (9)$$

where J_{kl} is an exchange integral, and s_k and s_l are the spin matrices of the kth and lth electrons. This expression was introduced by Dirac,[2] and it gives the impression of being a justification of the Heisenberg method, and the use of exchange integrals, on a sufficiently general basis so that we are led to ask if it avoids the difficulties with the Heisenberg method, pointed out in the preceding section. We shall see when we examine it that it does not avoid these difficulties, and that it does not in fact form a valid starting point for a complete theory of magnetism.

If we examine Dirac's derivation of the expression (9), we see that it was set up for problems of spin degeneracy. That is, for a problem of n electrons, we start with a set of orbitals $u_1\cdots u_n$ involving coordinates only, not necessarily all different, and consider the various functions of coordinates and spin which can be made up from them by assigning spins in all possible ways to these orbitals. In such a set of functions of coordinates, it is clear that any function, on account of the exclusion principle, can be identical with at most one other function. Each pair of identical functions must be occupied with an electron of each spin. If there are n' remaining functions, each appearing once, each one can appear with either spin, so that there are $2^{n'}$ ways of arranging spins. The problem of spin degeneracy then involves the $2^{n'}$ determinantal wave functions arising in this way. Dirac's operator is set up so as to give the same matrix components of energy between these $2^{n'}$ states as the correct Hamiltonian operator used with the determinantal method, provided the orbitals $u_1\cdots u_n$ are orthogonal. It does not give matrix components between different configurations, that is, between two determinantal functions corresponding to different sets of u's, and it does not give correct values if the u's are not orthogonal.

These limitations, though clearly pointed out by Van Vleck,[3] are generally glossed over. It is clear, however, that the method based on (9) is more specialized than the determinantal method. In the first place, it cannot rigorously be used for the Heitler-London or Heisenberg methods, for we have pointed out that the nonorthogonality of wave functions is essential to these methods. The approximation, often made, of assuming that it can be used in these cases, with an exchange integral J_{kl} given by (3), which can have either sign, is on exactly the same basis as the approximation which we have already dismissed as invalid in Sec. I, of writing the diagonal energy as the Coulomb energy minus the sum of all exchange integrals J_{kl}, of computing these by Eq. (3), and of disregarding overlap integrals. If we use really orthogonal orbitals, it is a correct starting point for discussing spin degeneracy; but we have just seen that in this case we must also consider configurational interaction with ionic states in which the Wannier functions are occupied by two electrons, and the Hamiltonian (9) is not able to describe these configurational interactions. Our feeling about this Hamiltonian (9) is thus very definite, and very adverse, as far as its application to magnetic problems is concerned: We believe that it has given a false and unjustifiable feeling of security to those who wished to use the Heisenberg method, and that in fact the uses which have been made of it are unjustifiable and incorrect. We do not feel that it is correct, in any way which has been justified from wave mechanics, to speak of exchange integrals between electrons in a crystal, in the Heisenberg sense, or to decide whether a substance should be ferromagnetic, or nonferromagnetic, or antiferromagnetic, on account of a positive or negative sign for such a hypothetical exchange integral. This criticism extends to the use of the term superexchange[13] in its relation to theories of antiferromagnetism; the derivation of this quantity, by Kramers, neglects orthogonality in just the same sort of way which we are objecting to in the present paper, and the writer sees nothing in the work on the subject which overcomes this difficulty in the use of the method. Before leaving the expression (9), we should point out that Serber[14] has shown how to remove the limitations which we have mentioned, i.e., that (9) demands orthogonal orbitals, and does not apply to configuration interaction; Anderson[13] uses some of these methods in his paper on superexchange, though he disregards nonorthogonality.

III. THE ENERGY-BAND THEORY OF FERROMAGNETISM

In the two preceding sections, we have endeavored to show that treatments of magnetism by the Heisenberg method are unjustified, and that if we try to overcome the difficulties of that method, we are led inevitably to the use of the determinantal method, with orthogonal one-electron functions or orbitals. If we have a complete orthogonal set of one-electron functions $u_i(x)$, involving coordinates and spin, we can pick n functions out of such a complete orthogonal set and form a determinantal function $(n!)^{-\frac{1}{2}}\det|u_i(x_j)|$. If we take all possible ways of picking out n one-electron functions from the complete orthogonal set, and set up all such determinantal functions, this will form a complete orthogonal set of antisymmetric functions of n electronic coordinates and spins, so that the correct wave function of the problem can be rigorously expanded in terms of them. For the one-electron functions, in a problem of a crystal, we may use the solutions of a periodic potential problem, which have the characteristics of Bloch waves; or we may use the Wannier functions arising from them. Since either type of function forms a complete orthogonal set, either one forms a proper starting point for a rigorous calculation. If we do not have exact solutions of the periodic potential problem, we can proceed as Mulliken[5] and others have done in the molecular problem, or as Löwdin[6] has done in discussing crystals: We can start with atomic orbitals and make orthogonal linear com-

---

[13] H. A. Kramers, Physica **1**, 182 (1934); P. W. Anderson, Phys. Rev. **79**, 350 (1950); J. H. Van Vleck, J. phys. et radium **12**, 262 (1951).

[14] R. Serber, Phys. Rev. **45**, 461 (1934).

binations of these atomic orbitals, either of the Bloch-like or Wannier-like type. The results of these calculations show that good results can be obtained in this way. The writer feels that our best hope at present of obtaining quantitative results for magnetic problems is to proceed in this way, using linear combinations of atomic orbitals, of an orthogonal nature, and calculating the energy of the crystal as Löwdin has done, but for both magnetized and unmagnetized states, comparing the energies of the two states.

The calculations of Mulliken and Löwdin mentioned above, and the usual applications of the molecular-orbital or energy-band method, are more specialized than we have indicated above. They are based on the use of a single determinantal wave function, formed from the *n* Bloch-like energy-band functions whose one-electron energies are lowest. The details of how to specify these one-electron energies involve a certain amount of subtlety, relating to problems of the Hartree-Fock equation, which we shall not go into here. We expect theoretically, and we find in practice, that a single such determinant gives a good description of an actual molecule or crystal at its observed internuclear distance. However, as the interatomic distances increase to infinity, it is well known that this single determinantal solution does not behave properly and that its asymptotic energy, at infinite internuclear distance, is too high. We have a situation shown schematically in Fig. 1, where the full curve shows the diagonal energy of the state represented as a single determinant, as a function of internuclear distance. The horizontal line is supposed to represent the correct energy of the system at infinite internuclear distance, and the dotted line represents the energy of the correct ground state, as determined by making linear combinations of determinants, as will be described later. It can then very well be that the single determinant forms quite a good approximation to the ground state near the minimum of the curve. It can also well be that we can independently determine the energy at infinite distance. Thus, the dissociation energy D can be well calculated from this single determinant, even though its energy at infinity is too high by the amount A. A solution like that shown in Fig. 1 is found in the simplest molecular problem, the H_2 molecule; a very similar situation is shown in Löwdin's[15] calculation of the sodium crystal, where he has been able to make a very good calculation of cohesive energy, even though his energy curve, like the full curve of Fig. 1, goes to much too high a value at infinity. Similar justification for this method of using a single determinant is provided by the calculations of Mulliken[5] and others mentioned earlier: they get good values for binding energies, from wave functions which would behave incorrectly at infinite distance.

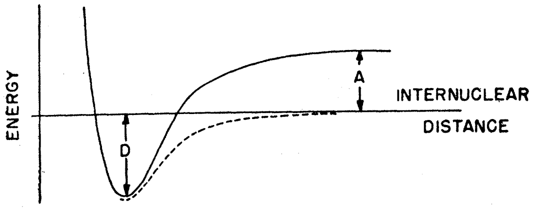

FIG. 1. Energy of single determinantal state formed from molecular orbitals (full curve), and correct energy of ground state (dotted curve).

For magnetic problems, however, this failing of the simple energy-band method using a single determinant, at large internuclear distances, can be serious; for it is well known that the *3d* orbitals concerned in magnetism are far apart in relation to their size, in ferromagnetic and more particularly in paramagnetic substances. Thus, we must look at the sort of situation described in Fig. 1, particularly at large distances, in a good deal more detail. First let us remind ourselves why the energy of the single energy-band determinantal function, given by the full curve in Fig. 1, is too high at infinite internuclear distance by the amount A. It is well known that this results because there is nothing in the wave function to keep electrons of opposite spin out of each other's way, and we are quite likely to find ionic states, in which positive or negative ions are found on some lattice sites rather than neutral atoms. Thus, in the H_2 problem, where the molecular orbital functions are $a\pm b$, the determinantal wave function corresponding to this state, as far as its orbital dependence is concerned, is $[a(1)+b(1)][a(2)+b(2)]=[a(1)b(2)+b(1)a(2)]+[a(1)a(2)+b(1)b(2)]$, a combination of the Heitler-London ground state, and of the Heitler-London ionic state, with equal coefficients. At infinite separation, there is a fifty percent chance that the wave function represents an ionic state. In computing the diagonal energy of the state, as shown in the full curve of Fig. 1, we then find terms representing the interaction of two electrons on the same atom, required to calculate the energy of the H^- ion. The energy A represents the energy required to form H^+ and H^- ions from the neutral H atoms, in the fifty percent of the cases where the ions are found, according to the determinantal wave function.

The situation described in Fig. 1 is for a state with no net magnetic moment. For investigating ferromagnetism, however, we must compare the energies of states of different magnetic moments; in a ferromagnetic problem, the lowest state will have a magnetic moment, and in a nonmagnetic case it will not. We next ask, therefore, how the energy of a single determinant, as a function of internuclear distance, depends on whether it represents a magnetic state or not. First, at small internuclear distances, where the energy band is broad, increase of magnetic moment will increase the energy, for in the nonmagnetized state each of the lowest one-electron energy levels will be occupied by two electrons, one of each spin, whereas in the magnetized state electrons of one spin (say −) are removed

---

[15] P.-O. Löwdin, J. Chem. Phys. 19, 1570, 1579 (1951).

from low-lying one-electron levels and are placed in higher unoccupied one-electron levels of the band of + spin. Thus, there is an increase of energy of the whole system, resulting from increased one-electron energies, the total amount being proportional to the band width, and hence increasing with decreasing internuclear distance. On the other hand, another effect works in the opposite direction, and persists to infinite separation, tending to lower the energy of the state of maximum magnetization below the unmagnetized state. This is the effect of exchange. The diagonal energy of a single determinantal state formed from orthogonal orbitals is the sum of the one-electron and Coulomb energies (these terms take care of the result of broadened energy bands just mentioned) minus the sum of exchange integrals J_{kl} of type given in Eq. (4), for all pairs of electrons with parallel spin. These exchange integrals are always positive; and when the orbitals u_i are Bloch functions, we find that at large nuclear separations they do not go to zero in the limit, but become interaction integrals between different electrons in the same atom. Thus, we have a set of such terms, coming in with negative sign, one for each pair of electrons with parallel spin. Now there are more such pairs for a magnetized state than for an unmagnetized state; thus, this exchange energy is lower for the magnetized state than the unmagnetized one.

The net result of these two effects, then, is that the energies of determinantal functions representing nonmagnetized and magnetized states formed from energy-band orbitals will look as shown schematically in Fig. 2. We can easily see why the energy of the magnetized state lies below that of the unmagnetized state, at infinite separation. This is on account of the incorrect tendency for electrons of opposite spin to get close together and form ions, in the determinantal wave function, as mentioned earlier. But electrons of the same spin are prevented from getting too close together by the exclusion principle. Thus, the greater the magnetization the fewer are the pairs of electrons which can improperly get together, and the smaller is the error. If the completely magnetized state happens to be one in which a band is just filled with electrons of + spin, with no electrons of − spin, then the exclusion principle by itself will entirely prevent ionic states, and the state of maximum magnetization will go to the correct energy at infinity. This is the case in H_2. It is also the case taken up by the writer[11] in a more detailed study of the present problem; this case is simple enough so that quantitative results can be obtained in computing the energy as a function of internuclear distance. A consideration of the exchange terms coming into the energy of the determinantal state, which as we have seen involve interaction between electrons on the same atom, shows that these are just the correct terms to describe this tendency of electrons of opposite spins in the unmagnetized state to form positive and negative ions.

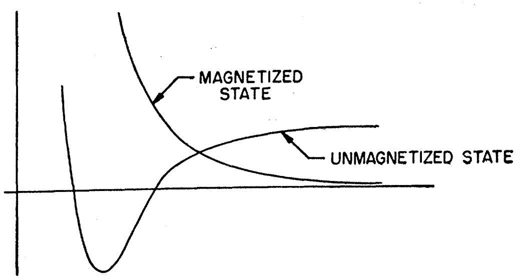

FIG. 2. Energy of single determinantal state formed from molecular orbitals for magnetized and unmagnetized states.

Now that we have considered the behavior of the energy of a single determinantal wave function formed from Bloch orbitals, both for magnetized and unmagnetized states, we can ask how the energies of the correct wave functions are related to them, for example, as indicated in the dotted curve of Fig. 1. From the case of H_2, and the magnetic case worked out by the writer in reference 11, we can tell the general lines which the discussion must take. To get good results, we must use many determinantal functions and solve a perturbation problem between them. If we are using Bloch functions as one-electron orbitals, we must use not only the determinant composed of the n lowest orbitals in the energy band concerned, but rather all determinants which can be formed from the orbitals in the whole band. We shall find an equal number of determinants formed from the Wannier functions of the band, provided we consider all the ionic Wannier states, which we have seen to be necessary from our discussion of Sec. I. The determinants formed from Bloch functions, or from Wannier functions, are found from each other by a unitary transformation, so that the same final result will be obtained by starting with either set. We must then solve the perturbation problem between these states, finding the set of resulting energy levels for each total spin. The lowest such energy level, for each total magnetization, will of course have to lie lower than the diagonal energy of the single determinantal function of the same magnetization indicated in Fig. 2. We can go further than this, however. At infinite internuclear distance, we shall of course have a paramagnetic sort of behavior, and the correct solution will have a very high degeneracy: The energy will be independent of the orientation of the magnetic moments of the separated atoms, so that the energy of the lowest state corresponding to each total magnetization, from the maximum to zero, will be the same. If, for instance, we have the simple case mentioned in the preceding paragraph, in which the state of maximum magnetization corresponds to no electrons of − spin, so that the energy of the single determinant is the correct energy value at infinite distance, we can be sure that the lowest energy level of zero magnetization will come at the same value at infinite distance. This situation is clearly shown in the calculation carried out in reference 11.

Let us now ask what the correct energy levels must look like, resulting from this calculation. For simplicity, we take the case just mentioned, where the wave function of the state of maximum magnetization is correctly given by a single determinant, though the general situation is not changed in any essential feature if we do not have this simplification. Then the correct energy of the unmagnetized states, as a function of internuclear distance, must have a form somewhat like that given by the dotted curve in Figs. 3(a) and 3(b). In both cases shown there, we have indicated that the dotted curve lies below the diagonal energy of the single determinant representing an unmagnetized state, but reduces to the same energy at infinity as the magnetized state. In the case of Fig. 3(a), the unmagnetized state everywhere has a lower energy than the magnetized, and the system must be nonmagnetic. In Fig. 3(b), on the other hand, the unmagnetized energy lies above the magnetized value at large internuclear distances and there is a region of distances over which the substance will be ferromagnetic.

There are many conclusions which can be drawn from these instructive figures. First, perhaps, is the nature of the energy difference between magnetized and unmagnetized states in the ferromagnetic problem, shown in Fig. 3(b). This energy difference is zero at infinity, increases as the internuclear distance decreases, goes through a maximum, then decreases to zero and changes sign at smaller internuclear distances. It is well known that there is much experimental evidence for this sort of behavior. In the language of the Heisenberg exchange integral, it has often been described by saying that one integral, for a ferromagnetic material, is positive for large internuclear distances, negative for smaller distances, just like the energy difference just described. We have already given reasons for feeling that the Heisenberg method is invalid, and that no exchange integral, of the Heisenberg or Heitler-London type, can be found which correctly represents the problem and shows the dependence on internuclear distance just described. It is clear, however, that the energy-band theory, when examined carefully, must necessarily lead to just the type of behavior which we have just described.

As a second point, if Fig. 3(b) represents the true state of affairs with any reasonable approximation, we see that the correct energy of the unmagnetized state will cross the energy of the magnetized state at an internuclear distance not far from that where the diagonal energy of the unmagnetized state crosses the energy of the magnetized state. In other words, the internuclear distance where the ferromagnetic interaction (a notation which might well replace "exchange integral") changes sign is given to a fair approximation by finding where the diagonal energies of the magnetized and unmagnetized energy-band functions cross. This is the reason, as pointed out in reference 11, why the estimates made by the energy-band method by the writer[16] as to which elements should be ferromagnetic were approximately correct, even though these estimates were based on a naive picture like that of Fig. 2.

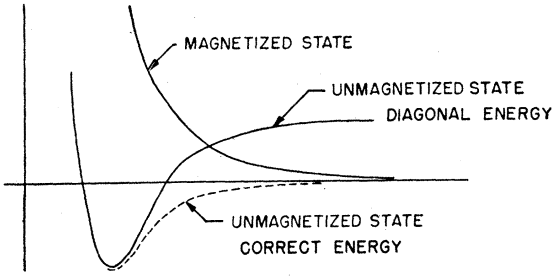

FIG. 3(a). Energy of single determinantal function, for magnetized and unmagnetized states, compared with correct energy of unmagnetized state (dotted curve), for nonmagnetic case.

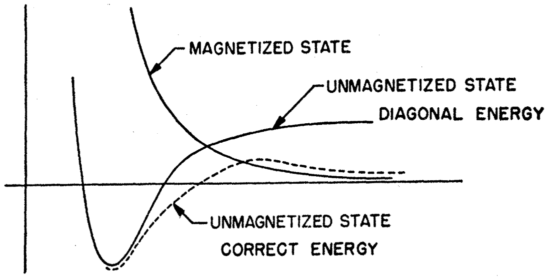

FIG. 3(b). Same as Fig. 3(a), for ferromagnetic case.

We may assume that the diagrams of Fig. 3 represent the energies of the $3d$ electrons. Superposed on this, of course, is the energy of the $4s$ electrons (which presumably have no significant magnetic effect). Since the $4s$ band is much broader than the $3d$, and its radius is much larger, this will result in a much deeper minimum of the energy curve than shown in Fig. 3(b), and at larger internuclear distances. Thus, we may expect curves like Fig. 4(a) and 4(b) to represent actual energy of the iron group elements as functions of internuclear distance. If the ferromagnetic interaction is positive at the minimum of the curve, as in Fig. 4(a), the substance will be ferromagnetic. If, however, the $3d$ orbital is of larger size, as in the earlier elements of the transition group, like Ti and V, then the ferromagnetic interaction will change sign at a larger internuclear distance and will be negative at the minimum of the curve, as in Fig. 4(b), so that the substance will be nonmagnetic, even though the interaction of $3d$ electrons is as shown in Fig. 3(b).

From Fig. 3(a) or Fig. 3(b), we may conclude that when the internuclear distance is small enough so that the diagonal energy of the unmagnetized state, as computed by the energy-band method, lies below that of the magnetized state, we cannot possibly have ferro-

---

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

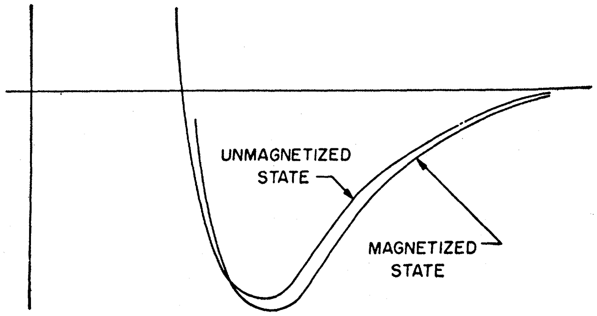

FIG. 4(a). Combined effect of $3d$ and $4s$ electrons, ferromagnetic case.

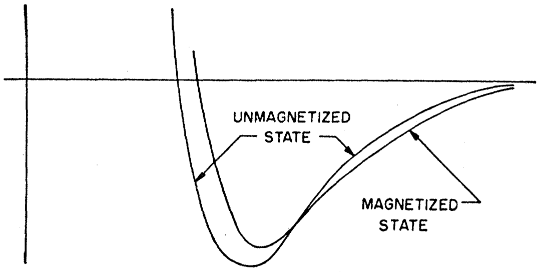

FIG. 4(b). Same as Fig. 4(a), nonmagnetic case.

magnetism. Furthermore, in this limit the true wave function of the unmagnetized state cannot lie far from the single determinantal wave function of the energy-band method. Thus, in such elements as Ti and V, we expect each individual atom to have zero magnetic moment, completely in contrast to the behavior of individual ions, but in agreement with the experimental results of Shull[17] and his collaborators. For cases where the $3d$ shell is smaller, however, we can say from the energy-band theory only that we can have either the case of Fig. 3(a) or Fig. 3(b). That is, the energy-band theory can show unequivocally that for substances with wide bands, ferromagnetism is impossible. For narrow energy bands, it can only show that it is possible; but it cannot distinguish, without more accurate calculations than have yet been made, whether ferromagnetism actually exists in these cases, or nonferromagnetism, or antiferromagnetism.

Let us finally take up the relation between our energy-band treatment of the problem and correlation energy. This term has been used to describe the decrease of energy when we go from an incorrect model of a metal, formed from a single determinant of Bloch-like functions, in which electrons of opposite spin can be found too close together, to a correct model in which the electrons of opposite spin are kept apart. Wigner and Seitz,[18] as is well known, have made estimates of the correlation energy for the alkali metals and have included a correction for this effect, which amounts to a large fraction of the cohesive energy. Löwdin,[6] on the other hand, has got very good numerical results for the cohesive energy of sodium, without using such a correction for correlation energy. Wohlfarth,[19] in private correspondence with the writer, takes essentially the position that at infinite internuclear distance the correlation energy represents just the difference between the full curve and the dotted curve of Fig. 1. That is, at infinite internuclear distance, it is the amount A indicated in Fig. 1. The writer agrees with this point of view; though the term "correlation energy" has meant so many things to different people that he feels it perhaps better not to use the word at all. If the correlation energy does in fact represent the difference between the two curves of Fig. 1, and if these curves really have something like the form shown there, then we should expect it to be a very small correction at the internuclear distance corresponding to the minimum of the curve of Fig. 1. This would be in accordance with the result of Löwdin, who got a very good result for a single determinantal wave function for sodium. It would not agree with the calculation of correlation energy of Wigner and Seitz, as given in reference 18. The writer is inclined to believe that this calculation of Wigner and Seitz represents a poor approximation, inapplicable at the minimum of the energy curve, and feels that the true correlation energy at the energy minimum is much smaller. The numerical accuracy of Wigner and Seitz's calculation of cohesive energy of sodium, using their correlation correction, is probably fortuitous.

Now let us consider the relation between correlation energy and the ferromagnetic interaction. The point of view of Wohlfarth[19] is that at finite internuclear distance there are two different effects: a correlation energy, and an exchange interaction which is responsible merely for the separation of the final magnetized and unmagnetized states, like the hypothetical Heisenberg exchange interaction. The writer disagrees with this point of view. From the general argument of the present paper, he feels that there can be no doubt as to the actual state of affairs. We must make our correlation correction, like that described with reference to Fig. 1, to reduce the energy of the unmagnetized state from the diagonal value coming from a single determinantal wave function, to the correct final value; that is, from the curve marked "unmagnetized state-diagonal energy" to that marked "unmagnetized state-correct value" in Fig. 3(a) or 3(b). We must make a similar but independent calculation for the magnetized state. In the particular case shown in Fig. 3, this correction is zero, but in general, where the completely magnetized state still has electrons of both spins, there will still be some correlation correction, though not as much as

---

[17] C. G. Shull and M. K. Wilkinson, Phys. Rev. 86, 509 (1952).

[18] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934); E. Wigner, Phys. Rev. 46, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).

[19] E. P. Wohlfarth, private correspondence.

for the unmagnetized states. Having carried out these calculations for both magnetized and unmagnetized states, we must then compare these final corrected energies; their difference will be the ferromagnetic interaction energy whose sign determines whether the metal is ferromagnetic or not. With this point of view, the correlation energy is inextricably tied up with the ferromagnetic interaction, and no independent calculation of the ferromagnetic interaction can be made; but it can be found only through the correlation energy calculation just described.

The detailed method of carrying out these calculations at large internuclear distance will not be described here. We have already mentioned one case[11] in which the writer has carried through such a calculation. A description of that calculation will illustrate the type of problems which will be encountered. The case taken up in reference 11 is that in which the magnetized state has a band entirely filled with electrons of + spin, with no electrons of − spin, so that it is expressed by a single determinant, as in the case illustrated in Fig. 3(a) and 3(b). The energy of this state was compared with that of a state which had just one electron of reversed spin. Effectively this consists of an electron in the otherwise empty band corresponding to − spin, and a hole in the otherwise filled band of + spin. The lowest diagonal energy of a single determinantal function representing this state is that in which the electron is at the bottom of the band of − spin and the hole is at the top of that of + spin; this corresponds to the energy marked "unmagnetized state-diagonal energy" in Fig. 3(a) or 3(b). The calculation corresponding to setting up the exact energy of the unmagnetized state involves setting up the lowest bound stationary state, in which the electron and hole are executing an oribt about their center of mass, similar to an exciton. This type of level has a lower energy, on account of the binding energy of the electron and hole. It was set up in detail in reference 11, and it was found that it led to an energy level of the correct sort. At infinite internuclear distance, it corresponded to the electron and hole being on the same atom; that is, to a state in which each atom of the crystal is neutral. As the internuclear distance decreased, the dimension of the "exciton" formed from the electron and hole increased, and its binding energy became less and less, until for a wide energy band the binding energy, which represents teh correlation energy, was negligible.

Under other circumstances the correlation energy comes, not from the attractive interaction of an electron and a hole, but from the repulsive interaction of two charges of like sign. Thus, a band almost filled with electrons of both spins (like the *d* band in Ni) will have a few vacancies, and they will tend to repel each other and stay out of each other's way. The calculation of either of these types of cases will remind us of the calculation of the behavior of electrons or holes near impurity atoms in a lattice of a semiconductor,[20] and like that problem, it is most easily handled in terms of Wannier functions. We shall not try to go further with these matters here; but it is the belief of the writer that it is only through such methods that we shall get a correct understanding not only of correlation energy, but also of the ferromagnetic interaction which in a satisfactory theory of magnetism will replace the inadequate concept of the Heisenberg exchange integral.

A beginning in the direction of such calculations has been made by Dr. A. Meckler,[21] who has calculated the structure of the O_2 molecule. He has set up atomic 1*s*, 2*s*, and 2*p* orbitals, for each atom, and has made orthogonal linear combinations of them. Then he has set up the $(12!)/(8!)(4!)=495$ determinants formed by assuming the 1*s* and 2*s* orbitals to be all occupied, but by assigning the remaining eight electrons, with both possible spins, in all possible ways to the remaining 12 orbitals (including spin). Of these 495 determinants, 9 have the symmetry characteristic of the $^3\Sigma$ ground state, and 12 of the next higher $^1\Sigma$ state. He has computed the matrix components of the Hamiltonian function between these determinants and has solved the resulting secular equations numerically on the Whirlwind digital computer at the Massachusetts Institute of Technology. This yields energy and wave functions for the ground state and the next excited state, as functions of the internuclear distance. Since all possible determinants are considered, the resulting energies and wave functions go into the best approximations to the ^3P ground state of the oxygen atoms at infinite separation. Meckler finds, as was to be expected, that the triplet state lies below the singlet. His calculated dissociation energy and internuclear distance for the ground state agree with experiment to about a percent, and the vibration frequency to a few percent. The values for the next excited state are not as accurate,

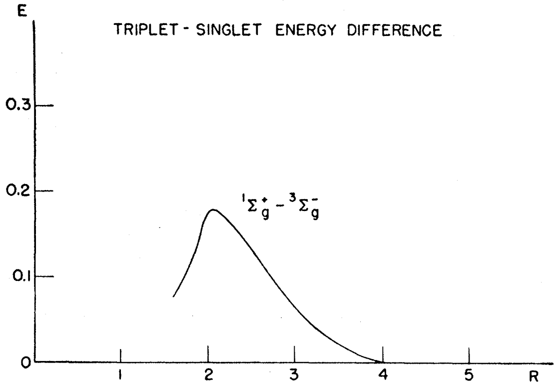

FIG. 5. Energy difference between magnetic and nonmagnetic state, for oxygen molecule, from calculation of Meckler.

---

[20] J. C. Slater, Phys. Rev. **76**, 1592 (1949).

[21] A. Meckler, Quarterly Progress Report on the Solid-State and Molecular Theory Group, M.I.T., July 15, 1952, and October 15, 1952.

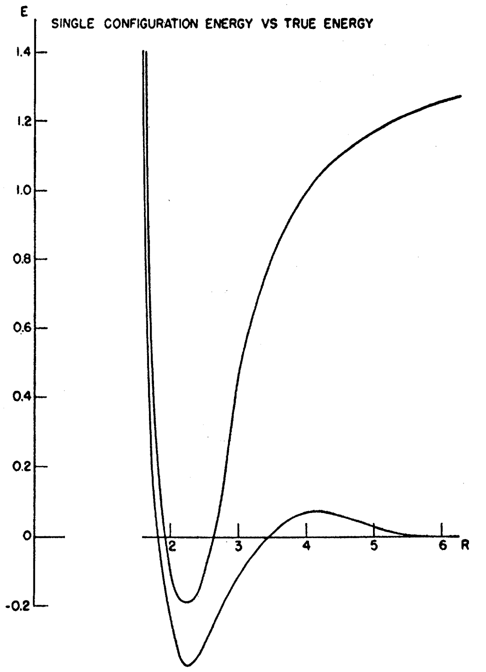

FIG. 6. Diagonal energy of molecular orbital state, compared with correct energy of ground state, for oxygen molecule, from calculation of Meckler.

but still are good approximations. The separation between singlet and triplet energies is shown in Fig. 5. It has the form which we have learned to expect of a ferromagnetic interaction energy, being zero at infinite distance, rising to a maximum, and then decreasing again at small distances, presumably changing sign at somewhat smaller distances than those for which the calculations are made. This, as far as the writer knows, is the first case where such a magnetic interaction has been directly calculated from Schrödinger's equation, using a correct molecular model.

It is interesting to compare the correct energy level of the ground state, as calculated by Meckler, and the corresponding diagonal energy of the molecular orbital state. This is shown in Fig. 6, and it is the specific application to this case of the general argument illustrated in Fig. 1. We see that the molecular orbital state, though it gives binding at internuclear distances of the right order of magnitude, is very inaccurate, and its energy rises much too high at large distances, as in Fig. 1. The diagonal energy of the triplet molecular orbital state, shown in Fig. 6, lies below that of the singlet molecular orbital state. This is in accordance with the prediction of Lennard-Jones,[22] one of the first deductions from the molecular orbital point of view. From Fig. 6, however, we see that the molecular orbital approximation is really quite bad here, and that it is very necessary to take linear combinations of a number of determinantal functions, as Mecker has done, and as we are advocating for the magnetic problem, in order to get good agreement with experiment.

---

[22] J. E. Lennard-Jones, Trans. Faraday Soc. 25, 668 (1929); see particularly p. 684.