

Magnetic Effects and the Hartree-Fock Equation*

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The Hartree-Fock equations state that each electron in an atom or molecular system should move in a different potential. In some cases, particularly magnetic cases, this leads to important consequences, since electrons with opposite spins move in different potentials. In particular, in an antiferromagnetic substance, electrons of + and - spin have different potentials; and for an electron of + spin, for instance, the potential energy is lower in those atoms whose spins are pointed in the + direction than in those with the opposite spin. This results in a periodic perturbation of potential, with periodicity twice the atomic periodicity, and leads to a splitting of each energy band in half, with a gap in the middle. In a case where the energy band was half full, resulting in a conductor: when we disregard this effect, the resulting half-band will be just filled when we consider it; this may explain the insulating nature of some antiferromagnetics. A similar argument applied to a diatomic molecule like H_2 can result in two alternative types of solutions of the Hartree-Fock equations: one leading to atomic orbitals, the other to molecular orbitals. The solution with atomic orbitals shows an analogy to the antiferromagnetic problem; that with ordinary molecular orbitals shows an analogy to the band theory of a non-magnetic conductor.

THE Hartree-Fock equations, as has been recently pointed out by the writer,¹ can be interpreted as ordinary Schrödinger equations for the one-electron wave functions or orbitals $u_i(x)$ out of which we can set up a determinantal wave function for an atom or molecular system. Each electron moves in a potential which is made up of the electrostatic fields of the nuclei and of all electrons, including itself, but with a correction because of the fact that the electron really does not act on itself. This correction takes the form of subtracting from the total charge density of all electrons an exchange charge density, representing a density whose total magnitude is one negative electronic charge concentrated, in general, about the electron in question. This exchange charge density, for the electron whose wave function is $u_i(x)$, takes the form

$$-e \sum_{k=1}^n \frac{u_i^*(x_1) u_k^*(x_2) u_k(x_1) u_i(x_2)}{u_i^*(x_1) u_i(x_1)}. \quad (1)$$

This charge density is located at point x_2 , and an integration must be carried out over this variable to find the corresponding potential at the point x_1 , where we are finding $u_i(x)$. In the reference just quoted, it was pointed out that often the exchange charge density does not depend in a very striking manner on the index i ; that is, almost the same potential can be used for the various wave functions. In such a case it was pointed out that it may be an advantageous simplification to replace (1) by a weighted mean over the various wave functions, securing, in this way, a single potential to use for all wave functions of the problem.

It is the purpose of the present note, on the other hand, to point out certain cases in which there is a very real advantage in using the different potentials for different wave functions indicated by (1). These cases seem to come up particularly when we are dealing with

magnetic problems. The wave functions u_i concerned in (1) are assumed to be functions of spin as well as coordinates; they are products of an ordinary coordinate wave function and the Pauli functions α or β of the spin coordinate. Thus, automatically, the product $u_i^*(x_1) u_k(x_1)$ is zero, unless functions i and k correspond to the same spin, so that the sum (1) really includes only terms coming from wave functions u_k whose spin quantum number is the same as that of u_i . Thus, it comes about that when there are not equal numbers of wave functions with + and - spins in a problem, the potential in which these two types of electrons move will be different. The difference is easily interpreted in a qualitative way from the results of the reference already quoted. There it was shown that the effect of the exchange potential is to depress the potential energy of the electron by an amount which depends on the local charge density of electrons: the greater this charge density, the lower the potential energy. Thus, if, for instance, there are more electrons of + than of - spin, the Hartree-Fock potential for an electron of + spin will be lower than that for an electron of - spin.

These differences in the potentials for electrons of the two spins will, of course, result in differences in the one-electron energies resulting from the solution of Schrödinger's equation and hence in energy terms in computing the diagonal energy of the state. These effects are familiar when we handle the exchange effect by perturbation methods. In finding the total energy, we must multiply (1) by $u_i^*(x_1) u_i(x_1)$ and integrate the resulting expression, multiplied by a potential energy function involving the coulomb expression $1/r_{12}$, over the coordinates of electrons 1 and 2. When we do this, we recognize the familiar exchange integrals coming from the perturbation treatment of multiplet theory, and the dependence on spin is the equivalent of the statement that exchange integrals occur only between pairs of electrons with the same spin. Thus, to the

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¹ J. C. Slater, Phys. Rev. **81**, 385 (1951).

extent that first-order perturbation theory is adequate, it makes no qualitative difference whether we use the Hartree-Fock exchange charge (1) in computing the exchange potential or merely use the Hartree equations without exchange. This freedom of choice is merely a statement of the theorem that the diagonal energy of a wave function is a correct energy up to second orders of small quantities; first-order modifications of the wave function, such as would come about if we used the Hartree instead of the Hartree-Fock equations, make only second-order errors in the energy. In many cases, of which the application to atomic multiplets is one, the situation is as just described, and the greatly added complication of using the Hartree-Fock rather than the Hartree method is not really justified by its results.

There are some cases, however, of which antiferromagnetism and covalent binding are two examples, in which a qualitative, and not merely a small quantitative, difference is found, depending on whether we use the Hartree-Fock method, with its different potentials for electrons of opposite spin, or not. The reason for this rather profound effect is that the magnetic modification of the potential in the Hartree-Fock case results in modification of the energy levels or energy bands of a type which would have to be described by second-order or higher order perturbation theory, and which would be missed entirely if we proceeded only by first-order perturbation theory, as in the usual theory of multiplet structure. The most striking example is in antiferromagnetism. We shall elaborate on this case in a moment; but, for the moment, let us consider a one-dimensional array of like atoms, each with the same number of electrons, but with the spins of the outer electrons pointing in the $+$ direction in one atom, $-$ in the next, and alternating in this way. Then the Hartree-Fock potential will have different values in alternate atoms, so that the period of the periodic potential will be two atoms for the Hartree-Fock potential, though it is only one atom for the ordinary Hartree potential. If we ask how the energy bands as calculated from the Hartree potential would be modified in going to the Hartree-Fock potential, we take advantage of our knowledge of the effect on energy bands of a perturbative potential with a period twice the lattice spacing: we know that the bands develop gaps in the middle, each band splitting into two, the half-bands holding half as many electrons per atom as the whole bands. If, then, we were dealing with the case where there were half enough electrons per atom to fill the complete band, the Hartree treatment would indicate a half-filled energy band, leading to a conductor, while the Hartree-Fock treatment would show the half-band to be filled, with an energy gap above, so that it would predict that the material would be an insulator. It is attractive to suppose that the fact that such antiferromagnetics as NiO and MnO are insulators rather than conductors may arise from such an explanation as this, though

they are far from being as simple as the one-dimensional case just described.²

It is easy to verify that the effect of going from the Hartree to the Hartree-Fock method in the example above arises from a higher order perturbation effect, if it is treated by perturbation methods. For we recall that when the effect of a periodic perturbing potential on energy bands is investigated, we find that this potential introduces interactions like those between an incident wave and a Bragg reflected wave. These interactions are a maximum when the incident and reflected wave have identical unperturbed energies (this corresponds to the position of the energy gap). This problem must be treated like a perturbation of a degenerate system; not even a second-order perturbation treatment is adequate. First-order perturbation methods, then, are completely inadequate to investigate such energy gaps, which nevertheless can have a great practical significance.

Let us look a little closer at this one-dimensional antiferromagnetic problem to analyze its nature more closely. For an electron of $+$ spin, the Hartree-Fock potential energy will be lower in those atoms which are known to have a net $+$ spin than in those of net $-$ spin. Each energy band will be split, as we have just mentioned, into two half-bands; but more than that, the wave function in the lower half-band will be concentrated largely in those atoms with $+$ spin, while the wave function in the upper half-band will be concentrated in those atoms with $-$ spin. The physical reason for the energy gap between the two half-bands is just the difference in average potential energy arising from this different charge distribution. If now we have only the lower half-band filled, the electrons will go largely into those atoms which were assumed from the beginning to have $+$ spin, thus verifying the self-consistent nature of the assumption about potentials. Similarly, the potential energy function for an electron of $-$ spin will be lower in the atoms with $-$ spin. The energy bands for such an electron will be identical with those for an electron of $+$ spin; but the wave functions in the lower half-band, which are occupied with electrons, will correspond to having the charge concentrated largely in the atoms with $-$ spin.

In the model which we have been discussing, the effect of the alternation of the Hartree-Fock potential from atoms with one spin to those with the other is to set up wave functions which are concentrated on atoms of one spin or the other. Thus, if the lower half-band is filled and the upper one is empty, the effect is the segregation of electrons of opposite spin, one from the other, so that they will not have random fluctuations of charge and will not lead to probabilities of ionic states. On the contrary, if we used the Hartree potential with a band half-filled with electrons, it is known that we have such fluctuations. The alternation of the Hartree-

² The difficulty of understanding the insulating nature of NiO has been pointed out by Mott, Proc. Phys. Soc. (London) **62**, 416 (1949) as a difficulty with the energy band theory.

Fock potential then has somewhat the same effect on the charge density that we get from the well-known Heitler-London method, as applied to the hydrogen molecule. To the extent that there is such a similarity, we agree with the remark of Mott² that in an insulator like NiO, we must use something more like a Heitler-London than an energy band picture. We may, in fact, examine the H₂ molecule from the point of view we have been describing for an antiferromagnetic and thus throw light on the relation of the Heitler-London method to the Hartree-Fock method. We shall see that they have similarities but are by no means identical.

Suppose we have two hydrogen atoms at a considerable distance from each other, and that we try to find a self-consistent solution by the Hartree-Fock method for the ground state, with one electron with each spin. We may first make the usual assumptions leading to symmetric or antisymmetric molecular orbitals. We assume that the wave function corresponding to the electron of each spin is either symmetric or antisymmetric in the midpoint of the nuclei, so that its charge density is symmetric. Then the exchange charge (1) will be symmetric, so that the Hartree-Fock potential for an electron of either spin is symmetric in the nuclei, and by the well-known solution of the two-potential problem the wave functions will be either symmetric or antisymmetric. Thus we have a self-consistent solution. On the other hand, suppose we start by assuming that the wave function corresponding to one spin will be concentrated on one nucleus and that of the other spin on the second nucleus, as in the antiferromagnetic problem. If the atoms are far enough apart so that the wave functions do not appreciably overlap, examination of the expression (1) then shows that the potential for an electron of + spin will be that of the two nuclei plus that of the electron of - spin; that is, this potential will be that of the free nucleus of the atom with + spin plus a neutral atom for that with - spin. Near the atom with + spin, the other neutral atom will exert no field, so that the Schrödinger equation will be just like that of a hydrogen atom, leading to an ordinary hydrogen wave function concentrated about that atom. Similarly, the Schrödinger equation for an electron of - spin will be that of a hydrogen atom at the other nucleus.

We see, in other words, that the solution of the Hartree-Fock equations is not unique in such a case, as has been surmised, for instance, by Seitz.³ One can, in fact, assume that the solution of the Hartree-Fock equation for H₂ can be approximated as a linear combination of the atomic functions *a* and *b* located on the two atoms; that is, one can assume that the function corresponding to the + spin is $c_{11}a + c_{12}b$, and that corresponding to the - spin is $c_{21}a + c_{22}b$. One then forms the energy integral, expressing it in terms of the *c*'s, and varies the *c*'s to make the energy stationary, subject to the condition that the wave functions remain normalized (which can be handled by the method of

undetermined multipliers).^{3a} When we do this, we find that the equations have two types of solutions. In all cases the symmetric or antisymmetric orbitals, corresponding to $c_{12} = \pm c_{11}$, $c_{22} = \pm c_{21}$, form a solution, but there are other solutions as well, which, at infinite separation, go to the limiting case $c_{11} = 1$, $c_{12} = 0$, $c_{21} = 0$, $c_{22} = 1$, or corresponding cases with the nuclei interchanged, but which depart more and more from these limits as the internuclear distance is decreased. This demonstrates in a simple case the existence of the two types of solution.

These atomic solutions that we have found are analogous to those which we described earlier for the antiferromagnetic case. They are not, however, identical with the Heitler-London description of the ground state of the molecule. If we recall the argument leading to the wave function by this method, we start with a function like that which we have been describing, corresponding, say, to having an electron of + spin on atom *a*, an electron of - spin on atom *b*; but we consider also the other state, degenerate with the first, with an electron of - spin on atom *a*, and one of + spin on atom *b*. The degenerate perturbation problem between these two states leads to two solutions: one the sum of these wave functions, the other the difference. One of these corresponds to the ground state, the other to the component of the triplet which has no spin along the axis with respect to which we are measuring spin. As we know from the Heitler-London method, these two states, the ground state and the triplet, lie far apart; and the two degenerate states which lead to them, and which lie roughly half-way between them, have energies approximately given by the Heitler-London coulomb energy, without the Heitler-London exchange energy. We know, however, that the exchange term is responsible for the major part of the binding in the ground state. Thus, the atomic type of wave function which we found in the preceding paragraph is not like the Heitler-London function for the ground state. We could not have expected that it would be. The perturbation problem of spin degeneracy is an essential part of the Heitler-London method, and the Hartree-Fock scheme, in which we definitely assign a spin to each wave function, cannot incorporate such an effect in a single wave function. If we wish to get the equivalent of the Heitler-London theory of valence for a complicated molecule, we must carry through the same treatment of spin degeneracy as in the conventional Heitler-London method, even though we start with wave functions derived from the Hartree-Fock method.

It is interesting to see in this way that the Hartree-Fock method can form the first step of a Heitler-London calculation. This is not, however, of any particular value in the solution of molecular problems. The great

³ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 251.

^{3a} The attention of the writer has been called by Prof. H. M. James to the fact that a similar (but not identical) calculation has been made by C. A. Coulson and I. Fischer, *Phil. Mag.* **40**, 386 (1949).

technical difficulty in the application of the Heitler-London method for complicated molecules is the non-orthogonality of the wave functions. It is true that the wave functions derived by the Hartree-Fock method can be proved to be orthogonal to each other, and this might seem to remove the difficulty. It does not, however; for the orthogonality of two Hartree-Fock functions corresponding to electrons of opposite spin arises from the spin part of the wave function, not from the orbital part. In the H_2 problem, for instance, the two atomic orbitals around atoms a and b are non-orthogonal, even if they are derived strictly by application of the Hartree-Fock method. Two Hartree-Fock atomic orbitals corresponding to electrons of the same spin, however, are necessarily orthogonal, and it is possible that this would make the Heitler-London method simple enough to make its use worthwhile.

It is interesting to consider the diagonal energy of the H_2 molecule according to the two types of Hartree-Fock approximations. At great distances, the atomic type of approximation will have a diagonal energy reducing properly to the sum of the energies of two neutral atoms; thus, it will lie below that of the molecular-orbital solution, which has an energy which is the average of the energy of two neutral atoms and the energy of a polar state consisting of a positive and a negative ion. As the distance decreases, however, this situation is reversed. The molecular-orbital solution approximates very closely the Heitler-London solution for the ground state at the actual internuclear distance in the molecule. On the other hand, as we have seen, the Hartree-Fock atomic approximation has an energy more like the coulomb Heitler-London energy, which does not lie nearly so low. Thus, we conclude that if we wish to use a single Hartree-Fock function, without further perturbation calculations, the atomic function is good at large values of internuclear distance, the molecular function at small values, and neither is very good in between.

We may now return to our antiferromagnetic case and ask whether it is as far from the truth as the atomic Hartree-Fock solution for H_2 . The answer will come by considering the spin degeneracy problem in the antiferromagnetic case. Here it is not immediately obvious what other arrangements of spin we are to consider, analogous to the simple interchange of spins between the two atoms in the Heitler-London model of H_2 . If we interchange all spins in a one-dimensional chain of alternating spins, we should find the nondiagonal matrix component of energy between the two states equal to zero to a very high order of approximation, on account of the very large number of electrons which would interchange spins in going from one function to the other. The only sort of function which would have an appreciable nondiagonal matrix component of energy from the state of alternating spins we start with would be one in which only a few spins are changed; for instance, we could modify the regular alternation $+-+--$ by interchange of two adjacent spins,

obtaining $+-+--$, for instance.⁴ To set up such a function, we might start with the regular Hartree-Fock problem of the alternating spins and treat the effect of the modified potential resulting from the interchanged spins as a local modification of the regular periodic potential. If we set up approximate solutions of this modified potential by superposing solutions of the periodic potential problem, we should presumably find that we had to use wave functions from the upper half-band in making up such a solution, and would certainly find that the diagonal energy of the modified state was different from that of the unmodified state. In fact, if the antiferromagnetic arrangement of alternating spins had a lower energy than the ferromagnetic arrangement where all spins are the same, this modified state would have a higher diagonal energy than the unmodified one.

In the antiferromagnetic problem, then, an interchange of spins changes the diagonal energy of a state, in contrast to the case of the H_2 molecule. As a result, the nondiagonal matrix component of energy will have a much less perturbing effect than in the molecule. Such a situation was found in reference 4, where the effect of spin degeneracy was found to be much less important in a crystal lattice than in a molecule. Hence, we may conclude that we commit a much smaller error in the antiferromagnetic case than in the molecule if we merely use the diagonal energy of a state with alternating spins as representing the real energy of the system.

There are many questions concerning antiferromagnetics, ferromagnetics, and related problems, which the present note does not answer. The most important one, which we have not even tried to answer, is that of which state has lower energy in a given crystal: the antiferromagnetic state, corresponding to alternating spins, and the half-band structure we have been describing; the random state, in which every atom on the average has as many $+$ as $-$ spins, so that we have the ordinary molecular orbital or energy band functions, with the possibility of charge fluctuations on the atoms; or the ferromagnetic state, which we have hardly mentioned, in which all atoms have spins of the same sign, so that the effect of the exchange terms in the Hartree-Fock equation is mainly to depress the potential energy, and energy levels, of those electrons with the same spin as the spin of the atoms, and to raise the energy of those with opposite spins. Rather than waiting until all these questions can be solved, however, it seems worthwhile to point out, in the present note, the close relation of the Hartree-Fock equations to these problems, and, in particular, to the problem of antiferromagnetism. That problem is one which ought to be amenable to the methods of energy bands, even though the attempts to treat it have, so far, been by modified Heitler-London methods.

⁴ This problem has been treated by the Heitler-London method by J. C. Slater, *Phys. Rev.* **35**, 509 (1930); H. Bethe, *Z. Physik* **71**, 205 (1931); and other writers.