

d^2p configuration have as parents all 6 terms of the dp configuration.

The total correction therefore will be of the form

$$2x\{(\mathbf{l}_{d_1} \cdot \mathbf{l}_p) + (\mathbf{l}_{d_2} \cdot \mathbf{l}_p)\} + 2y\{(\mathbf{s}_{d_1} \cdot \mathbf{s}_p) + (\mathbf{s}_{d_2} \cdot \mathbf{s}_p)\} + 2z(\mathbf{l}_{d_1} \cdot \mathbf{l}_{d_2}).$$

This may be transformed into the form

$$\begin{aligned} &x\{L(L+1) - L'(L'+1) - l_p(l_p+1)\} \\ &+ y\{S(S+1) - S'(S'+1) - s_p(s_p+1)\} \\ &+ z\{L'(L'+1) - 2l_d(l_d+1)\} \\ &= xL(L+1) + yS(S+1) + (z-x)L'(L'+1) \\ &\quad - 2x - \frac{3}{2}y - 12z - yS'(S'+1). \end{aligned}$$

L, S refer to the d^2p terms and L', S' refer to the parent terms of the core. Since we are interested only in the relative positions of the terms, we may include the constant part $(-2x - \frac{3}{2}y - 12z)$ of the correction in the parameter A . The part $-yS'(S'+1)$ may be included in the parameter C because the coefficient of C in all the known terms of d^2p has the form $S'(S'+1)$.

The final correction to each term $d^2(S'L')pSL$ is therefore

$$\alpha L(L+1) + \beta S(S+1) + \gamma L'(L'+1);$$

$(\alpha = x, \beta = y, \gamma = z - x).$

TABLE III. Variation of parameters in the isoelectronic sequence.

Parameter	Ca I	Sc II	Ti III	V IV	Cr V	Mn VI
F_2	88	259	450	588	719	851
G_1	327	371	439	518	599	681
G_3	-101	2	48	79	105	132
x	59	100	34	28	34	42
y	-491	-111	48	142	220	312

In Table I are listed the results of fitting our formulas to the terms of Ti II and Ni II by the method of least squares. The mean deviations are 140 cm^{-1} in Ti II and 130 cm^{-1} in Ni II. In Table II are listed the values of the corresponding parameters.

We also fitted the set of parameters F_0, F_2, G_1, G_3, x, y , to the experimentally known terms of the dp configuration of the Ca I isoelectronic sequence. The results are listed in Table III. We found a regular variation of y with the degree of ionization. The parameter x remained almost constant except for a jump at Sc II. It is worth noting that the dp interaction parameters of Ti II are much nearer to those of Sc II than to those of Ti III.

Lastly I wish to thank Professor G. Racah for suggesting this problem to me and for his constant help and advice throughout all the stages of the work.

Unrestricted Hartree-Fock Method*

GEORGE W. PRATT, JR.

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts

(Received December 16, 1955)

The unrestricted Hartree-Fock method is based upon the use of a single-determinant total wave function in which orbitals of the same n, l , and m_l values but different m_s values are regarded as being independent. The differences which arise between such orbitals are discussed. It is shown, using the Li atom as an example, that these differences are not merely a result of using a single determinant which has improper symmetry, but arise when the full spin-degeneracy problem is carried through. Conclusions for Li are generalized to more complicated systems. The influence of the unrestricted Hartree-Fock method on the calculation of magnetic form factors, its influence on hyperfine interactions, and its bearing on antiferromagnetism is pointed out.

INTRODUCTION

THE quantum-mechanical description of atomic structure is based upon the representation of a many-electron system by the one-electron approximation in which the total state is described as a linear combination of determinants of one-electron functions. These orbitals are labeled by four quantum numbers and it is generally assumed that functions of the same n and l are related by the L^+, L^-, S^+ , and S^- operators. Nesbet¹ has introduced the term equivalence restriction

to which the above assumption belongs. It is the purpose of this paper first to point out that the best one-electron functions may not necessarily be those for which all functions of the same n, l , and m_l are *always* related by the S step-up and step-down operators, and secondly to compare various methods of handling the problem when the equivalence restriction is relaxed. The case of the Li atom is taken as an example; for this case it is shown that the variational equations do not imply the equality of any pair of one-electron functions. Arguments are given which

* The research in this document was supported jointly by the United States Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

¹ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955). A number of writers have mentioned the possibility of using

different orbitals for different spins when the total wave function is a single determinant. See, for example, P. O. Löwdin, Phys. Rev. **97**, 1509 (1955) and references cited there.

indicate that the best one-electron functions obtained from an unrestricted treatment will not be very different from those found from the restricted method. If these small differences are neglected in diagonalizing L^2 and S^2 , one arrives at the unrestricted Hartree-Fock method. It is shown for Li that an approximate treatment of L^2 and S^2 does not lead to serious error and in less favorable cases corrections could be made by perturbation theory.

The result for Li can be generalized to the case of N electrons of the same spin outside an M -electron core. Two orbitals of the M -electron core u_i and u_i' which have the same n, l , and m_l values and which are treated as being independent are found to have different exchange interactions with the N outer electrons. This is interpreted as an exchange polarization of the inner M electrons by the outer electrons. It is shown that these terms arise when the full spin-degeneracy problem is treated, in which no spatial orbital is associated with any particular spin but all associations are used. This leads to the important conclusion that the differences in orbitals associated parametrically with different spins, which arise from the unrestricted Hartree-Fock method for systems of nonzero spin, are not merely a result of disregarding the spin degeneracy problem but are of a fundamental nature.

Important changes in the total energy and one-electron charge densities are to be expected in a system of large net spin and an improvement over the equivalence restriction is anticipated. These corrections may be of importance in getting better agreement with magnetic form factors as found by neutron diffraction,^{2,3} fine structure, and hyperfine structure splittings.⁴ The exchange polarization effect may play an important role in antiferromagnetic substances, as pointed out by Slater.⁵ In another paper a self-consistent field calculation is reported for the Fe atom, in which the one-electron functions having different parametric spin dependence in a single determinant state are varied separately.

STATEMENT OF THE PROBLEM

In order to find the best one-electron functions for a many-electron system, one finds the average energy of the system with respect to some approximate many-electron wave function ψ which is made up of one-electron orbitals u_i . This average energy is varied with respect to the u_i , resulting in a set of coupled integro-differential equations. The solution of these equations gives the best u_i , consistent with the form of the starting total wave function. If ψ is simply a product of the u_i , the variational equations are known as the Hartree equations. If ψ is a single determinant of the u_i , the

variational equations are known as the Hartree-Fock equations.

There are certain requirements which the form of the total wave function must satisfy according to the Hamiltonian H of the problem. The first is that ψ be antisymmetric with respect to the interchange of the labels of any two particles; this requirement is satisfied by the Hartree-Fock method. If the total L^2 and S^2 commute with H , then ψ must be an eigenfunction of these operators. This last requirement is usually taken to hold for atomic systems, but it can only be satisfied by a single determinant in special cases.

The restricted Hartree-Fock approach consists of writing down a single determinant of the u_i , where i stands for a set of four one-electron quantum numbers n, l, m_l , and m_s . One now varies the average energy only with respect to those u_i 's with different n and l values. This involves the implicit assumption that all functions which have the same n and l quantum numbers but different m_l and m_s values are not independent, but are related by the L^+ , L^- , S^+ , and S^- operators. The unrestricted Hartree-Fock method drops this assumption and one now separately varies all of the orbitals u_i with different i . If we are interested mainly in spin effects, we could regard all of the orbitals with the same n, l , and m_s values as being related by the L^+ and L^- operators, but drop the S^+ and S^- relationship.

Now suppose that the unrestricted Hartree-Fock approach has been adopted, except that the L^+ and L^- relationships are assumed to apply to all orbitals. The starting ψ is a single determinant in which all u_i 's with different n, l , or m_s values are assumed to be independent. If the total $M_s \neq 0$, the variational equations for orbitals associated with α spin will have a different appearance from those equations for orbitals of β spin. The differences arise in the exchange terms, for now these summations only over orbitals of parallel spin will have different forms for the two spin directions. The question which this paper attempts to answer is whether the differences which come from such a treatment have any physical significance or whether they are simply the result of neglecting the spin degeneracy problem. These remarks are best illustrated by the example of the Li atom.

THE LITHIUM ATOM

According to the prescription of the unrestricted Hartree-Fock method, the starting ψ for the Li atom would be

$$\psi = A \{ u_{1s\alpha} u_{1s'\beta} u_{2s\alpha} \}, \quad (1)$$

where A is the antisymmetrizing operator and all of the u_i 's are to be varied separately. Since there is no exchange interaction between $1s'$ and the other orbitals, it will have a different type of variational equation than the orbitals associated with α spin. Therefore, $1s$ and $1s'$ are not related by the S^+ and S^- operators and

² Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

³ D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 126 (1954).

⁴ Abragam, Horowitz, and Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

⁵ J. C. Slater, Phys. Rev. **82**, 538 (1951).

we are led to different charge densities due to the $1s$ and $1s'$ orbitals. It is to be noted that in taking the u 's to be eigenfunctions of the one-electron S_z operator, the u 's must have the form of a product of a space function and a spin function. By only considering one determinant in the starting ψ , a parametric spin dependence is introduced into the spatial part of the u 's, because $1s$ is always associated with α spin and $1s'$ with β spin.

Now the question is whether or not the difference in charge densities of $1s$ and $1s'$ has any real meaning, i.e., whether the difference arises simply from the fact that in our total wave function we have neglected the two other possible determinants,

$$A\{u_{1s}\beta u_{1s'}\alpha u_{2s}\alpha\} \quad (2)$$

and

$$A\{u_{1s}\alpha u_{1s'}\alpha u_{2s}\beta\}. \quad (3)$$

If these determinants are mixed into the starting ψ so as to have an eigenfunction of S^2 , the parametric spin dependence will disappear and perhaps the difference between $1s$ and $1s'$ along with it.

The answer to this question can be had by going through the complete treatment of the spin degeneracy problem for Li, which we will now proceed to do. The one-electron orbitals will be denoted by u_{1s} , $u_{1s'}$, and u_{2s} . They are assumed to be normalized, independent, but not necessarily orthogonal. The branching diagram indicates that there are two linearly independent states of $S^2 = \frac{3}{4}$ and one state of $S^2 = 15/4$. Only the $S^2 = \frac{3}{4}$ case is dealt with here, since this corresponds to the ground state of Li. The two linearly independent $S^2 = \frac{3}{4}$ states are

$$\phi_1 = A\{(u_{1s}\alpha u_{1s'}\beta u_{2s}\alpha) - (u_{1s}\beta u_{1s'}\alpha u_{2s}\alpha)\}, \quad (4)$$

and

$$\phi_2 = A\{2(u_{1s}\alpha u_{1s'}\alpha u_{2s}\beta) - (u_{1s}\alpha u_{1s'}\beta u_{2s}\alpha) - (u_{1s}\beta u_{1s'}\alpha u_{2s}\alpha)\}. \quad (5)$$

These states are not properly normalized due to the lack of orthogonality between the u 's. The starting ψ for the variational method is a linear combination of ϕ_1 and ϕ_2 with coefficients A_i to be determined variationally. Thus

$$\psi = A_1\phi_1 + A_2\phi_2, \quad (6)$$

apart from correct normalization.

The Hamiltonian is taken to be

$$H = \sum_i \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{e^2 z}{r_i} \right\} + \sum_{i>j} \frac{e^2}{r_{ij}}, \quad (7)$$

or

$$H = \sum_i H_0(q_i) + \sum_{i>j} H_{ij}(q_i, q_j).$$

The average energy corresponding to (6) is

$$\begin{aligned} E_{L, s} = E_{0, \frac{3}{2}} = & \sum_i \langle i|i \rangle + \sum_{i>j} \langle ij|ij \rangle \\ & + (|A_1|^2 - |A_2|^2) \{ (1s\ 1s'|1s'\ 1s) \\ & - \frac{1}{2}(1s\ 2s|2s\ 1s) - \frac{1}{2}(1s'\ 2s|2s\ 1s') \} \\ & + \{ A_1^* A_2 + A_1 A_2^* \} \{ (1s\ 2s|2s\ 1s) \\ & - (1s'\ 2s|2s\ 1s') \} + \text{other terms due to} \\ & \text{nonorthogonality of the } u\text{'s.} \quad (8) \end{aligned}$$

The symbol $\langle i|i \rangle$ is the average of $H_0(q_i)$ defined in (7) with respect to the i th orbital. The symbol $\langle ij|kl \rangle$ is

$$\langle ij|kl \rangle = \int \int u_i^*(q') u_j^*(q) H(q, q') u_k(q') u_l(q) dq' dq. \quad (9)$$

Without even considering the terms due to non-orthogonality in (8), it will be seen that each of the three one-electron functions appears in $E_{0, \frac{3}{2}}$ in a different way. In particular the $1s$ and $1s'$ orbitals have a different exchange interaction with u_{2s} , as is shown in the last term of (8). The variational equations for the u 's will each be of different form and will in general have distinct solutions. Therefore, it is seen that the full spin-degeneracy treatment does lead to different $1s$ and $1s'$ orbitals. This different exchange interaction of the $1s$ and $1s'$ electrons is referred to as exchange polarization of these orbitals by the $2s$ function. Of course, by allowing the $1s$ and $1s'$ orbitals to be independent an additional degree of variation is introduced and a lower total energy may well be achieved.

THE UNRESTRICTED HARTREE-FOCK METHOD FOR Li

The starting point for this treatment is the single determinant (1). The average energy with respect to this state is

$$E = \sum_{i=1}^3 \langle i|i \rangle + \sum_{i>j} \langle ij|ij \rangle - (1s\ 2s|2s\ 1s), \quad (10)$$

where $i=1$ stands for u_{1s} , $i=2$ for $u_{1s'}$, and $i=3$ for u_{2s} as before. It is well known that, except for the simplest systems, it is a practical necessity to have the one-electron functions orthonormal. This is very conveniently achieved in the unrestricted method. Those orbitals with different parametric spin dependence are orthogonal through spin association. Since the total wave function is a single determinant, any linear combination among the rows leaves the determinant invariant. Therefore, those orbitals not orthogonal by spin can be orthogonalized at no expense to the total energy. These orbitals will henceforth be taken as orthonormal without loss of generality.

We note in the average energy (10) that the $1s$ orbital has an exchange interaction with u_{2s} , but that the $1s'$ orbital has no such interaction because of its

opposite parametric spin dependence. Therefore, the charge densities for the $1s$ and $1s'$ orbitals will again be different. The general equation for a spatial orbital with α -spin association coming from a single determinant with x α spins and y β spins as well as the equation for an orbital with β spin can easily be written. A Slater⁶ averaging procedure can be carried out with the result that there is a single average potential for all electrons of α spin and another average potential for those of β spin.⁷

It is possible to estimate the extent of the differences between orbitals of the same n and l but different m_s which arise from the unrestricted Hartree-Fock approach. Suppose a set of orbitals has been obtained for a system by the restricted Hartree-Fock method. The orbitals of the unrestricted method can be expanded in terms of these functions. Differences between orbitals assumed to be the same in the restricted method correspond to admixing excited configurations of the restricted orbitals. For the inner electrons this would involve the admission of highly excited states, which will have a very small weight in the final wave function. Therefore, the inner orbitals of the same n and l but different m_s will be very much alike while important differences may arise for the outermost functions.

If the charge densities and energies which come from the unrestricted Hartree-Fock method are to be of any significance, the single-determinant total wave function must be as close to a pure state as possible. One has to consider the mixing in of other possible determinants. If this effect is large, then the single-determinant description will be unreliable and the spin-degeneracy problem must be resolved. The unrestricted Hartree-Fock approximation may well furnish a satisfactory set of one-electron functions for generating all other determinants in this case.

The consequences of not diagonalizing S^2 for Li must now be examined. The state

$$\psi_2 = A \{u_{1s}\beta u_{1s'}\alpha u_{2s}\alpha\} \quad (11)$$

is nearly degenerate with (ψ_1) (Eq. 1) and the improvement in the energy obtained by mixing these states must be calculated. Since (1) and (11) are not orthogonal to each other, the resulting final energy is

$$E = \frac{E_0 + \frac{1}{2}\epsilon - H_{12}\Delta_{12}}{1 - \Delta_{12}^2} \pm \frac{1}{(1 - \Delta_{12}^2)} [(H_{12} - E_0\Delta_{12})^2 + \epsilon\Delta_{12}(E_0\Delta_{12} - H_{12})]^{\frac{1}{2}}, \quad (12)$$

where $E_0 = H_{11}$, $H_{22} = E_0 + \epsilon$, and $\Delta_{12} = (\psi_1, \psi_2)$. Assuming that the differences in the $1s$ and $1s'$ orbitals will be small, then Δ_{12} will be nearly minus one, ϵ will be a small number, and H_{12} will be nearly equal to $-H_{11}$. Neglecting the second term in the square root of (12),

⁶ J. C. Slater, Phys. Rev. **81**, 385 (1951).

⁷ G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).

we have

$$\begin{aligned} E_{S=0} &= (E_0 - H_{12}) / (1 - \Delta_{12}) \sim E_0, \\ E_{S=1} &= (E_0 + H_{12}) / (1 + \Delta_{12}) \sim 0, \end{aligned} \quad (13)$$

where $E_{S=0}$ and $E_{S=1}$ are the energies corresponding to the singlet formed by the difference of (1) and (11) and the triplet formed by their sum respectively. Hence, for Li there will be no important lowering of the energy due to the neglected determinant (11) and the single-determinant approximation is not a poor description of the atom from this point of view.

It is apparent that if $1s$ and $1s'$ are nearly identical, then the state (1) is nearly an eigenfunction of S^2 . The average value of S^2 with respect to (1) is

$$(\psi_1^*, S^2 \psi_1) = (7/4) - \Delta_{12} - \Delta_{13} \sim \frac{3}{4}, \quad (14)$$

where

$$\Delta_{13} = \{(u_{1s}\alpha u_{1s'}\beta u_{2s}\alpha)^*, (u_{1s}\alpha u_{1s'}\alpha u_{2s}\beta)\} \sim 0.$$

If the equivalence restriction is invoked for Li, the two independent $S = \frac{1}{2}$ states (4) and (5) coalesce into a single determinant

$$A \{w_1\alpha w_1\beta w_2\alpha\}. \quad (15)$$

Since there are only two independent orbitals, there will be only two variational equations, which are

$$\begin{aligned} & \left\{ H(q) + \int w_1^*(q') H(q, q') w_1(q') dq' \right. \\ & \quad \left. + \int w_2^*(q') H(q, q') w_2(q') dq' \right\} w_1(q) \\ & - \frac{1}{2} \left\{ \int w_2^*(q') H(q, q') w_1(q') dq' \right\} w_2(q) \\ & = \lambda_{11} w_1(q) - \frac{1}{2} [w_2^* w_2^* / w_1 w_2] w_2(q), \quad (16) \end{aligned}$$

and

$$\begin{aligned} & \left\{ H(q) + 2 \int w_1^*(q') H(q, q') w_1(q') dq' \right\} w_2(q) \\ & - \left\{ \int w_1^*(q') H(q, q') w_2(q') \right\} w_1(q) \\ & = \lambda_{22} w_2(q) - [w_2^* w_2^* / w_1 w_2] w_1(q). \quad (17) \end{aligned}$$

The λ_{ij} stand for the Lagrangian parameters introduced in order to satisfy an orthonormality constraint on the w 's which cannot impair the energy since the total state is a single determinant. The points of interest in this treatment are that the λ_{ij} matrix cannot be diagonalized and that the equation for the doubly occupied orbital w_1 has a basically different form from the equation for the single occupied function w_2 . These are general features of the equivalence restriction.⁸

SUMMARY AND CONCLUSIONS

We have set out here to examine the meaning of the unrestricted Hartree-Fock method, which leads to

⁸ L. Brillouin, Actualités sci. et ind. No. 159 (1934).

different spatial functions for orbitals of the same n and l but different spin associations. The question is whether or not this difference is a consequence of neglecting the spin degeneracy problem. Examination of the complete treatment for Li indicates that the $1s$ and $1s'$ spatial functions will not be the same. If the differences are neglected as far as diagonalizing S^2 , we get the single determinant of the unrestricted method. Since the differences in the $1s$ and $1s'$ orbitals arise through unequal exchange interactions, this is termed exchange polarization.

The conclusions for Li can be extended readily. Consider an atom which under the equivalence restriction would be described as having a $2M$ -electron core of M doubly occupied orbitals and with N outer electrons of parallel spin. The atom is in an $S^2 = \frac{1}{2}N(\frac{1}{2}N+1)$ state and is here a single determinant. Consider any two orbitals in this determinant with the same n , l , and m_l values but with different m_s . Let the equivalence restriction now be relaxed for these two orbitals so that their spatial parts are independent. Then they can be combined to form a singlet and a triplet

$$u(nlm_l)\alpha u(n'lm_l)\beta \pm u(nlm_l)\beta u(n'lm_l)\alpha. \quad (18)$$

By combining these two states with the $2M-2+N$ electrons which are in an $S^2 = \frac{1}{2}N(\frac{1}{2}N+1)$ state, we can form two $(2M+N)$ -electron states ϕ_1 and ϕ_2 of $S^2 = \frac{1}{2}N(\frac{1}{2}N+1)$. The total wave function for the system will be a linear combination of ϕ_1 and ϕ_2 analogous to (6) in the Li case. The average total energy will contain a matrix component of H between these states which is

$$\begin{aligned} (\phi_1 H \phi_2) = \text{Const} & \sum_{i=1}^N \text{over the } N \text{ outer electrons} \{ (u(nlm_l)u_i | u_i u(nlm_l)) \\ & - (u(n'lm_l)u_i | u_i u(n'lm_l)) \} \\ & + \text{terms due to nonorthogonality.} \quad (19) \end{aligned}$$

Again we see that $u(nlm_l)$ and $u(n'lm_l)$ ⁹ have a different exchange interaction with the outer electrons, which implies different variational equations and solutions for the orbitals. The equivalence restriction has only been relaxed for two core orbitals to reach this conclusion, but the result would not be impaired if the equivalence restriction were relaxed for all core functions at once. It is also clear that this exchange polarization will affect the rest of the core.

The unrestricted Hartree-Fock method is an approximate treatment of the problem when the equivalence restriction is not enforced. It not only offers a practical escape from the very complicated spin-degeneracy problem, but makes use of spin to avoid orthogonality

⁹ In abandoning the equivalence restriction, it has been necessary to introduce an additional label for the u 's which has been a prime. Perhaps a more convenient notation would be a superscript, e.g., $u^{(i)}(nlm_l)$.

difficulties. It is of course recognized that by carrying out a sufficiently extensive configuration interaction based on the equivalence restriction, one can obtain as good a description of a system as desired. The merit of the unrestricted method is that it deals directly with the exchange polarization effect.

There are a number of problems in which exchange polarization may play an important part. Atomic charge densities of paramagnetic atoms as found by neutron diffraction do not seem to be in good agreement with calculated densities.^{2,3} In the Fe calculation to be reported in another paper, better agreement was obtained. It would be interesting to see how far the exchange polarization effect would go in explaining the s -electron effect in hyperfine structure. Mn^{++} should show no hyperfine structure if it were truly represented by the $3s^2, 3d^5$ equivalence restriction state. The observed splitting is attributed to very small amounts of unpaired s -electrons and an attempt has been made to resolve this problem by a configuration-interaction treatment based on the equivalence restriction.^{4,10} The unrestricted method would give the result that the magnetic field at the nucleus due to the inner s -electrons would not be exactly self-canceling as happens with the equivalence restriction, resulting in a small hyperfine splitting. This field at the nucleus due to the inner s -electrons arises not only for the single determinant, unrestricted state but also for the state of proper spin symmetry. The correct spin state (6) for Li gives for the average value of the operator $\sum_{i=1}^3 \delta(r_i) S_{zi}$, the expression

$$\begin{aligned} 2|A_1|^2 |U_{2s}(0)|^2 + 2|A_2|^2 \{ 2|U_{1s}(0)|^2 + 2|U_{1s}'(0)|^2 \\ - |U_{2s}(0)|^2 \} + 2\{A_1^* A_2 + A_2^* A_1\} \{ |U_{1s}'(0)|^2 \\ - |U_{1s}(0)|^2 \} + \text{terms due to nonorthogonality.} \end{aligned}$$

The relation of the unrestricted Hartree-Fock method to antiferromagnetism has been discussed by Slater.⁵ The exchange potential energy of an electron has a different periodic behavior than that of the chemical structure and this can cause the energy bands to split thereby changing the electrical properties of such substances. The present paper points to the conclusion that the different exchange potentials for electrons of different spin have a rigorous origin and are not simply the result of an over-simplified treatment. The unrestricted approach using a single averaged potential for all electrons of α spin and another average potential for all electrons of β spin appears to be a very attractive means of discussing magnetic problems.

ACKNOWLEDGMENTS

Part of this work was done while the writer was a member of the Solid State and Molecular Theory Group at M.I.T. It is a pleasure to acknowledge the stimulation received from the members of that group and especially by its director, Professor J. C. Slater.

¹⁰ M. Sachs, Phys. Rev. **90**, 1058 (1953).