PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Orbital Self-Consistent-Field Theory.
III. Hamiltonian for the Natural Orbitals of Multiconfigurational Wave Functions*

William H. Adams
School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903,†
and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 20 May 1968; revised manuscript received 12 March 1969)

A self-consistent-field Hamiltonian which determines the natural orbitals of a multiconfigurational wave function, is derived. The advantage of using natural orbitals in multiconfigurational wave functions is that one can then determine the Langrangian multipliers once and for all. The Hamiltonian is valid for almost all of the proposed multiconfigurational wave functions, including those for which self-consistent-field equations have not been previously given. The Hamiltonian is derived by combining the results of Parts I and II of this series of studies. It is derived in such a way that it contains explicitly electronic Coulomb and exchange operators. This has the advantage that the coupling operators which appear in the Hamiltonian, depend only on that part of the two-electron density matrix which describes the correlation between the electrons. The practical question of how to use the derived equation is discussed in a brief, general way.

1. INTRODUCTION

Natural orbitals are the key to deriving a single, one-electron Hamiltonian valid for all of the natural orbitals in nearly all of the proposed multiconfigurational self-consistent-field theories. Natural orbitals at once place these various theories on a common base, allow one to solve in every case for the same orbitals and to determine once and for all the undetermined off-diagonal Lagrangian multipliers and the coupling operators, but yet introduce no operators more complicated to construct in a computer than those that usually appear in self-consistent-field theories. The derivation of the one-electron Hamiltonian is straightforward, requiring only refinement of the variational principle discussed in II,[1] and the union of the natural-orbital equation of Paper II with the equations of Paper I.[2] The last is accomplished by a method I have discussed in detail elsewhere.[3]

A multiconfigurational (MC) wave function Ψ for an N-electron system, is a linear combination of determinants D_K of N spin orbitals ψ_μ each.

$$\Psi = \sum_K C_K D_K[\psi] .$$

The C_K are usually determined by requiring that they minimize the total energy. The set of M spin orbitals, $M > N$, are the occupied spin orbitals. Any spin orbital orthogonal to all M occupied orbitals is an unoccupied or virtual orbital. An MC self-consistent-field (SCF) wave function is one in which the energy has been extremalized both with respect to the C_K and to the ψ_μ. This extension of the Hartree-Fock theory was first suggested and investigated by Frenkel[4] in a second-quantized formulation. A number of general studies of MC SCF theory have been published[2, 5–8] since Frenkel's.

There are two defects from which nearly every proposed multiconfigurational theory suffers. One defect is that nearly every orbital is determined by its own distinct Hamiltonian. A second defect is the appearance of numerous undetermined Lagrangian multipliers. The first is a practical defect in that it complicates the problem of deciding which orbitals are occupied, by requiring one to decide which orbitals determined by which Hamiltonian are occupied. (I also feel that it is an aesthetic defect to have more than one Hamiltonian determine the orbitals.) The second is a defect until the Lagrangian multipliers are determined so as to guarantee that the total energy is extremalized. In many cases the Lagrangian multipliers have been left undetermined. The first defect was one from which my reformulation of MC SCF theory in I did not suffer, unlike the other general formulations. However my formulation like the others, did have the second defect when applied to a restricted MC SCF theory, i.e., one in which the C_K are restricted in some way, or in which not all determinants that can be constructed from M occupied orbitals, are used. In this paper the Lagrangian multipliers are determined by introducing natural orbitals.

The introduction of natural orbitals (NO) into MC SCF theory at first sight should appear to be of little value. The use of NO's will not improve the quality of the MC SCF wave function. The MC SCF orbitals extremalize the energy calculated with an MC wave function so that for a given number of orbitals and configurations, the best (lowest) energy is found. If the MC SCF orbitals are transformed into NO's of that wave function the energy is not changed. The value of the NO's is that they make it possible to determine the Lagrangian multipliers once and for all in the form of coupling operators akin to those introduced in open-shell Hartree-Fock theory by Roothaan.[9] A bonus of formulating the various restricted MC SCF theories in terms of NO's is that in each theory one is then solving for approximations to the same functions, the exact NO's of a system. Surprisingly, in most restricted MC SCF theories it is an advantage to work with NO's.

The role of NO's in restricted MC SCF theories is indicated in Sec. 2 in a concise survey of the many proposed theories. Section 3 unifies the energy extremalization considerations of I and II. In Sec. 4 the derivation of an MC SCF natural spin orbital (NSO) Hamiltonian is sketched. In Sec. 5 a Hamiltonian for NO's is determined in which the electronic Coulomb and exchange operators are explicitly introduced. Section 6 is devoted to more or less practical questions concerning the complexity and usefulness of the derived equations. In the final section my conclusions are stated.

2. RESTRICTED MC SCF THEORIES

Many restricted MC SCF theories have been proposed since Frenkel's general study.[4] A feature that nearly all of them have in common is that they may be conveniently formulated in terms of NO's. It is my purpose here to review briefly the various proposals, indicating in each case how NO's enter, whether or not the SCF equations have been given and the off-diagonal Lagrangian multipliers determined, and whether or not the orbitals are determined by a single, one-electron Hamiltonian.

The first restricted MC SCF theory seems to have been introduced and used by Hartree, Hartree, and Swirles.[10] They carried out calculations on the oxygen atom in which the interacting configurations differed from each other in at least two orbitals. Recently this approach has been used and/or reformulated by several investigators.[11–14] The restriction that the interacting configurations be at least doubly excited with respect to one another, automatically makes the calculated orbitals, natural orbitals. In each of the formulations thus far given there is an additional Hamiltonian for each symmetry orbital not having the maximum occupation number for that symmetry. The Lagrangian multipliers have been correctly determined in these cases.

Another approach to the practical use of MC SCF theory is that suggested by Yutsis and explored by him and his co-workers.[15] The essential simplification in Yutsis approach depends upon one C_K being close to unity and the rest close to zero in magnitude. He then retains in the equations for the orbitals only those terms which are linear in the large C_K. This means that the orbitals that satisfy his SCF equations only approximately extremalize the energy. In this paper I am interested primarily in those approaches in which the SCF equations exactly determine the orbitals which extremalize the energy.

A different kind of restricted MC SCF theory was proposed by Hurley, Lennard-Jones, and Pople.[16] They recognized that the chief defect of the Hartree-Fock SCF theory was that it did not allow for correlation between electrons of opposite spin. In fact the Hartree-Fock theory imposes a wrong-way kind of correlation by requiring that the spatial parts of most of the up-spin and down-spin orbitals be identical. Hurley, Lennard-Jones, and Pople suggested that this defect could be eliminated by using two-electron functions – geminals – instead of paired orbitals. They showed also that if a strong orthogonality condition were imposed between the geminals, the resultant energy expressions were not very much more complicated than in the Hartree-Fock case. Later it was shown by Arai[17] that the strong orthogonality condition implied that each geminal could be expanded in terms of sets of orbitals, and that the orbitals appearing in the expansion of one geminal were orthogonal to those appearing in the expansion of any other strongly orthogonal geminals. One consequence of this property is that the NSO's constructed from each geminal are also the NSO's of the N-electron wave function.[18] On this basis Kutzelnigg derived SCF equations for the NSO's of Hurley, Lennard-Jones, and Pople wave functions.[18] He found a different Hamiltonian for each orbital. In addition a large number of undetermined Lagrangian multipliers in his equations have been approximated by setting them equal to zero.

A generalization of the Hurley, Lennard-Jones, and Pople approximation was proposed by McWeeny.[19] Instead of constructing an N-electron wave function from strongly orthogonal two-electron functions, McWeeny suggested using also functions of three, four, or more, electron coordinates. These strongly orthogonal group functions can also be expanded in terms of orbitals, the orbitals of any one group function being orthogonal to those of any other group function.[17] An SCF version of this theory has been given by Klessinger and McWeeny[20] for a product of strongly orthogonal group functions. The SCF equations for the orbitals were given only for the case in which the basis set used for the orbitals of any group function are orthogonal to all of the basis functions of all of the other group functions. This is a practical procedure, but it offers no assurance that the energy is extremalized with respect to the mixing of orbitals between the group functions. And there is of course at least one SCF equation for each group. A perturbative approach to pair functions based on the strong orthogonality condition has also been given,[21] but it is not pertinent to this study.

Still another approach to restricted MC SCF theory was proposed by Löwdin.[22] This method approximates the N-electron wave function by a single determinant of spin orbitals. Each spin orbital is pure up or down spin, but the spatial parts of the spin orbitals are not paired as in the Hartree-Fock theory. In order to have spin eigenfunctions the determinant is spin projected. Löwdin has called this the method of different orbitals for different spins (DODS). Kotani generalized Löwdin's approach.[23a] Recently Goddard[23b] has studied in detail the same methods, and has carried out calculations. The natural orbitals for DODS wave functions have been formally derived by Harriman.[24] From Harriman's work, it appears that natural orbitals are a very convenient set to use in the construction of DODS wave functions. A restricted form of the DODS method, the alternant molecular orbital method, was also proposed by Löwdin[22, 25] and has been studied extensively.[26] In this case the natural orbitals again can play a central role. The SCF formulation of the alternant molecular orbital method has not been given before.

Several researchers have adopted a pragmatic approach to the problem of calculating NO's. Edmiston and Krauss[27] have introduced pseudonatural orbitals which should yield almost self-consistent wave functions. Aesthetically "almost" is not entirely satisfactory. In addition the lack of an SCF equation for the NO's is disturbing, since such an equation should be useful.

In recent work of Bender and Davidson[28] can be criticized also for not offering an SCF equation for NO's. These authors have coupled a configuration interaction (CI) program with a program to analyze the CI function for NO's. The resultant NO's are used with new basis functions to find a new CI wave function, and so on to self-consistency in a suitable number of NO's. One benefit of an SCF NO equation would be to remove the necessity of dealing with the extra configurations needed in the Bender-Davidson approach. A further criticism of their approach is that it does not guarantee that the energy is extremalized with respect to the NO's. The resultant error in the energy should nevertheless be small.

It has been suggested that an MC wave function constructed from Slater determinants of nonorthogonal orbitals would be more rapidly convergent than one in which orthogonal functions were used.[8a] It is probably a valid suggestion. Such a wave function can also be expanded in terms of Slater determinants of orthogonal orbitals, but it requires many more configurations than when nonorthogonal orbitals are used. Both Gilbert,[8a] and Benston and Chong[8b] have derived the basic MC SCF equations in the case of nonorthogonal orbitals. Gilbert leaves the multipliers undetermined, and Benston and Chong use a method which does not correctly eliminate them. It is not clear that NO's would be of any value when nonorthogonal orbitals are used in forming the MC wave functions.

One conclusion to be drawn from this review is that nearly every restricted MC SCF theory thus far suggested has been or could have been conveniently based on natural orbitals. A second conclusion is that the MC SCF methods thus far proposed yield different equations for different orbitals. A final conclusion is that for only two cases have the Lagrangian multipliers been determined; the case in which all pairs of determinants are at least doubly excited relative to each other, and in Goddard's version of DODS.

3. ENERGY EXTREMALIZATION

In MC SCF theory there are three independent variations to be considered when one requires the orbitals to be orthonormal. These variations change the C_K, mix the M occupied orbitals with orbitals orthogonal to all of the occupied orbitals, and mix the M occupied orbitals among themselves. The variation of the C_K yields the well-known equations of the CI method. The variation that mixes occupied orbitals with unoccupied orbitals was considered in I. The variation that mixes the occupied orbitals with each other was treated in II in the case that the orbitals were the complete set of NSO's. In this section I shall generalize somewhat the results of Paper I, and I shall specialize somewhat the results of II to the case of a finite set of NSO's.

In Paper I only the minimization of the energy of the lowest energy state of given symmetry was considered explicitly. Upper bounds to the energies of a set of excited states will automatically come out of the secular equations. To get the lowest possible upper bound to the energy of an excited state, however, the energy of that state must be extremalized. This is possible if the energy of the state in question corresponds to one of the roots of the secular equation which determines the MC SCF wave function. It was pointed by Shull and Löwdin[29] that since the roots of the secular equation could always be numbered in order of increasing energy, and since the nth root is then an upper bound to the true energy of the nth lowest state,[30] the nth root of the secular equation may be minimized. Thus the MC SCF equations derived in I are valid for those excited states corresponding to roots of the secular equation, as well as to the lowest energy state.

The specialization of the variational principle for NSO's given in II is relatively minor. In Paper II I pointed out that the energy of any state of a system would be an extremal with respect to the mixing of the complete set of NSO's when the C_K were fixed. In MC SCF theory one deals only with a finite set of NSO's. Thus according to the arguments of the preceding paragraph, the *n*th root of the secular equation of MC SCF theory must be a minimum with respect to the mixing of the NSO's with the C_K fixed, since the *n*th lowest root is always an upper bound to the *n*th lowest energy level.

The two variations of the orbitals treated in I and II can now be combined in deriving an effective Hamiltonian for the NSO's or NO's of any state corresponding to a root of the secular equation. There is no reason however to believe that the NO's of one MC SCF state are equal to those of another, or even that they are simply related.

4. NATURAL SPIN-ORBITAL HAMILTONIAN

I stated in Paper II that the NSO equation I had derived there did not in itself appear to be of great practical value. However, using essentially the same approach the problem of determining the undetermined, off-diagonal Lagrangian multipliers of restricted MC SCF theory,[2] can be neatly solved. The result is a master equation for the NSO's of MC SCF theories. The derivation requires an important but straightforward modification of the operators $\underline{m}$ and $\underline{N}$ of II, and the unification of the resulting effective Hamiltonian with the one discussed in I.

Before going through the derivation, it is important to recall what the off-diagonal Lagrangian multiplier problem of MC SCF theory is. The essential point is that the total energy in MC SCF theory must be extremalized with respect to two distinct kinds of variations of the orbitals. In I only one kind of variation of the occupied orbitals was satisfactorily handled. This was the one that mixed occupied orbitals with unoccupied (virtual) orbitals. I gave in Paper I the basic equations that must be satisfied if the occupied orbitals are to extremalize the energy with respect to that kind of variation. In Sec. 6 of I it was pointed out that the resultant equation did not extremalize the energy with respect to variations that mixed the occupied orbitals among themselves, and that in the case of a restricted MC SCF theory there were Lagrangian multipliers yet to be determined. This second kind of variation is the same kind that was considered in II. In this section I use the method of II to determine the Lagrangian multipliers for all those restricted MC SCF theories which can be formulated in terms of NSO's or NO's.

The unitary transformation operator $\underline{U}$ defined in Eqs. (3.1) and (3.2) of II requires only one modification to make it directly applicable in MC SCF theory. The modification is necessary to guarantee that $\underline{U}$ mixes only occupied orbitals. The definition of $\underline{U}$ uses the fundamental invariant $\underline{\rho}$, which was defined in I in terms of the *M* occupied orthonormal spin orbitals ψ_μ.

$$\underline{\rho}=\sum_{\mu=1}^{M}|\psi_\mu\rangle\langle\psi_\mu|. \tag{4.1}$$

The operator for the unitary mixing of the occupied orbitals is

$$\underline{U}=\underline{1}+\epsilon\underline{\rho}\,\underline{m}\,\underline{\rho}, \tag{4.2}$$

where $\underline{m}$ is required to be anti-Hermitian, and $\langle\psi_\mu|\underline{m}^\dagger\underline{m}|\psi_\nu\rangle$, finite. Otherwise $\underline{m}$ is arbitrary. The variation of *E* can now be carried out as in II. Note that the normalizations and symbols used in this paper, unless otherwise indicated, are the same as used in I and II. One exception is the use of underlines instead of boldface for operators. The conventions of transformation theory are adopted.

The first variation of *E* due to operating on the occupied orbitals with $\underline{U}$ from Eq. (4.2), must vanish if the energy of the state considered is to be a minimum with respect to unitary transformations of the occupied orbitals. The equation that results from this requirement is in the MC case just Eq. (3.8) of II projected onto the Hilbert space of occupied orbitals.

$$\underline{\rho}_1[\underline{\gamma}_1\underline{h}_1-\underline{h}_1\underline{\gamma}_1+\mathrm{Tr}_2(\underline{\Gamma}_{12}\underline{v}_{12}-\underline{v}_{12}\underline{\Gamma}_{12})]\underline{\rho}_1=0. \tag{4.3}$$

If this condition is satisfied then the MC SCF energy is minimized with respect to the mixing of the occupied orbitals. Equation (4.3) and Eq. (2.15) of I completely specify the orbitals that minimize the total energy in MC SCF theory. The two conditions are easily coupled together to give a single, Hermitian, one-electron Hamiltonian.

Equation (4.3) can be replaced by an eigenvalue equation within the Hilbert space of occupied orbitals in the same way that Eq. (3.9) was replaced by Eqs. (3.15) in II. Define the operator $\underline{N}_1$ by its matrix elements with respect to the occupied NSO's ψ_μ.

$$\langle\psi_\mu|\underline{N}_1|\psi_\nu\rangle=(\gamma_\mu-\gamma_\nu)^{-1}\times\langle\psi_\mu|\mathrm{Tr}_2(\underline{\Gamma}_{12}\underline{v}_{12}-\underline{v}_{12}\underline{\Gamma}_{12})|\psi_\nu\rangle. \tag{4.4}$$

I showed in Paper II that $\langle\psi_\mu|\underline{N}_1|\psi_\nu\rangle=0$ for $\mu=\nu$, and for $\gamma_\mu=\gamma_\nu$, when the equality was due to symmetry. The operator $\underline{N}_1$ can be expanded in terms of the occupied orbitals only.

$$\underline{N}=\sum_{\substack{\mu\neq\nu\\ \gamma_\mu\neq\gamma_\nu}}^{\mathrm{occ}}|\psi_\mu\rangle\langle\psi_\mu|\underline{N}|\psi_\nu\rangle\langle\psi_\nu|. \tag{4.5}$$

The equation analogous to Eq. (3.15) of II is

$$\underline{\rho}(\underline{\mathrm{h}}+\underline{\mathrm{N}})\underline{\rho}\psi_\mu=\epsilon_\mu\psi_\mu\,. \tag{4.6}$$

It is this equation that I wish to combine with the equation derived in I.

The basic condition arrived at in I was [see Eq. (2.15)]

$$(\underline{1}-\underline{\rho}_1)\,(\underline{\mathrm{h}}_1\underline{\gamma}_1+\mathrm{Tr}_2\underline{\mathrm{v}}_{12}\underline{\Gamma}_{12})\underline{\rho}_1=0. \tag{4.7}$$

Since $\underline{\rho}\,\underline{\gamma}=\underline{\gamma}\,\underline{\rho}=\underline{\gamma}$, Eq. (4.7) can be put into a form that readily combines with Eq. (4.6). First define an inverse to $\underline{\gamma}$ in the sense used in I, i.e.,

$$(\underline{\gamma})^{-1}\underline{\gamma}=\underline{\gamma}\,(\underline{\gamma})^{-1}=\underline{\rho}\,. \tag{4.8}$$

For NSO's $(\underline{\gamma})^{-1}$ is easily constructed. Then as in I multiply Eq. (4.7) from the right by $(\underline{\gamma})^{-1}$ to get

$$(\underline{1}-\underline{\rho}_1)[\underline{\mathrm{h}}_1+\mathrm{Tr}_2\underline{\mathrm{v}}_{12}\underline{\Gamma}_{12}(\underline{\gamma}_1)^{-1}]\underline{\rho}_1=0\,. \tag{4.9}$$

Define the non-Hermitian operator

$$\underline{\mathrm{G}}=(\underline{1}-\underline{\rho}_1)\mathrm{Tr}_2\underline{\mathrm{v}}_{12}\underline{\Gamma}_{12}(\underline{\gamma}_1)^{-1}\,. \tag{4.10}$$

Equation (4.9) implies that

$$(\underline{\mathrm{h}}+\underline{\mathrm{G}}+\underline{\mathrm{G}}^\dagger)\psi_\mu=\underline{\rho}(\underline{\mathrm{h}}+\underline{G}+\underline{\mathrm{G}}^\dagger)\underline{\rho}\psi_\mu=\underline{\rho}\,\underline{\mathrm{h}}\underline{\rho}\psi_\mu \tag{4.11}$$

since $\underline{\rho}\,\underline{\mathrm{G}}=\underline{\mathrm{G}}^\dagger\underline{\rho}=0$. Equation (4.11) is the basic equation of MC SCF theory.

Equation (4.11) can be combined with Eq. (4.5). (The procedure is the same one I have used in the derivation of localized orbital equations equivalent to the usual Hartree-Fock equations.[3]) Substitution of $\underline{\rho}\,\underline{\mathrm{h}}\underline{\rho}\psi_\mu$ from Eq. (4.6) into Eq. (4.11) gives

$$(\underline{\mathrm{h}}+\underline{\mathrm{G}}+\underline{\mathrm{G}}^\dagger)\psi_\mu=\epsilon_\mu\psi_\mu-\underline{\rho}\underline{\mathrm{N}}\underline{\rho}\psi_\mu\,.$$

Thus if I define the effective Hamiltonian to be

$$\underline{\mathrm{F}}=\underline{\mathrm{h}}+\underline{\mathrm{N}}+\underline{\mathrm{G}}+\underline{\mathrm{G}}^\dagger \tag{4.12a}$$

the MC SCF equation for NSO's is

$$\underline{\mathrm{F}}\psi_\mu=\epsilon_\mu\psi_\mu\,. \tag{4.12b}$$

I have replaced $\underline{\rho}\underline{\mathrm{N}}\underline{\rho}$ by $\underline{\mathrm{N}}$ in Eq. (4.12a) since from the definition of $\underline{\mathrm{N}}$ it follows that $\underline{\mathrm{N}}\underline{\rho}=\underline{\rho}\underline{\mathrm{N}}=\underline{\mathrm{N}}$. Equation (4.12) involves no undetermined Lagrangian multipliers. The operator $\underline{\mathrm{N}}$ defined in Eqs. (3.4) and (3.5), is akin to the coupling operator of open shell Hartree-Fock theory.[9]

To derive Eq. (4.12) I have had to introduce $(\underline{\gamma})^{-1}$ and thus exploit one of the liberties which, I pointed out in Paper I, can be taken with Eq. (2.15) of I, without changing its meaning. The operator $\underline{\mathrm{F}}$ defined above can itself be modified by exploiting some of the other liberties that can be taken with the basic equations of MC SCF theory. These liberties were also noted in I. I believe that these liberties can be profitably and practically exploited. In Sec. 5, I explicitly exploit one such freedom.

5. NATURAL-ORBITAL EQUATION

Up to this point in this paper and in I and II, I have been interested in formal aspects of MC SCF theory almost exclusively. With this section I begin to consider the theory from the computational viewpoint. Computationally it is more convenient to deal with spinless quantities, so in this section I give the one-electron Hamiltonian for NO's. Also computationally it should be advantageous to reduce the importance of the operators $\underline{\mathrm{N}}$ and $\underline{\mathrm{G}}$. This is accomplished by exploiting some properties of MC SCF theory noted in I.

The switch from using NSO's and spin-dependent density matrices to NO's and spinless density matrices is straightforward. The first step is to integrate out the spin in the equation for E and substitute the spinless one-body and two-body density matrices, $\underline{\mathrm{p}}_1$ and $\underline{\mathrm{P}}_{12}$, respectively.

$$\mathrm{Tr}\,\underline{\mathrm{p}}_1=N, \qquad \mathrm{Tr}\,\underline{\mathrm{P}}_{12}=N(N-1)\,, \tag{5.1}$$

$$E=\mathrm{Tr}\,\underline{\mathrm{h}}_1\underline{\mathrm{p}}_1+\tfrac{1}{2}\mathrm{Tr}\,\underline{\mathrm{v}}_{12}\underline{\mathrm{P}}_{12}\,. \tag{5.2}$$

Now let the ψ_μ be NO's rather than NSO's. The variation of the NO's can be carried out as with the NSO's, the equations equivalent to Eqs. (4.12) can be derived for the NO's. Rather than do that here, I first want to modify the two-electron contribution to E in such a way as to decrease the importance of $\underline{\mathrm{N}}$ and $\underline{\mathrm{G}}$.

The modification to be made was in part discussed in I. There I broke Γ_{12} into a correlated and an uncorrelated part using the usual definitions, i.e., I wrote $\underline{\Gamma}_{12}=\underline{\gamma}_1\underline{\gamma}_2+\underline{\mathrm{g}}_{12}$. If there is no correlation between the electrons, then $\underline{\Gamma}_{12}$ is by definition equal to $\underline{\gamma}_1\underline{\gamma}_2$. I argued in Paper I that this separation should be useful. Now I break $\underline{\mathrm{P}}_{12}$ down in a similar fashion in order to reduce the importance of $\underline{\mathrm{N}}$ and $\underline{\mathrm{G}}$. This time however, I introduce exchange explicitly. The decomposition is best given in the coordinate representation. (The coordinates of electron i are denoted by x_i.)

$$\langle x_1x_2|\underline{\mathrm{P}}|x_1'x_2'\rangle=\langle x_1|\underline{\mathrm{p}}|x_1'\rangle\langle x_2|\underline{\mathrm{p}}|x_2'\rangle$$
$$-\tfrac{1}{2}\langle x_1|\underline{\mathrm{p}}|x_2'\rangle\langle x_2|\underline{\mathrm{p}}|x_1'\rangle+\langle x_1x_2|\underline{\mathrm{g}}|x_1'x_2'\rangle\,. \tag{5.3}$$

The second term on the right is the exchange term. A partial justification for this decomposition can be found in the Hartree-Fock theory and in the theory of strongly orthogonal group functions.[19]

In studying strongly orthogonal group functions and density matrices McWeeny found an interesting result. Let the superscripts R and S on density matrices denote specific groups. McWeeny[19] showed that for an antisymmetrized product of strongly orthogonal group functions having $M_S=0$, where M_S is the eigenvalue of the z component of the spin operator,

$$\underline{p}=\textstyle\sum_R \underline{p}^R , \tag{5.4}$$

$$\begin{aligned}\langle x_1 x_2|\underline{P}|x_1 x_2\rangle &= \textstyle\sum_R \langle x_1 x_2|\underline{P}^R|x_1' x_2'\rangle \\ &+ \sum_{R\neq S}\sum [\langle x_1|\underline{p}^R|x_1'\rangle\langle x_2|\underline{p}^S|x_2'\rangle \\ &- \tfrac{1}{2}\langle x_1|\underline{p}^R|x_2'\rangle\langle x_2|\underline{p}^S|x_1'\rangle].\end{aligned} \tag{5.5}$$

An expression for the $\underline{g}_{12}$ of strongly orthogonal group functions is found by combining Eqs. (5.3), (5.4), and (5.5).

$$\begin{aligned}\langle x_1 x_2|\underline{g}|x_1' x_2'\rangle &= \textstyle\sum_R [\langle x_1 x_2|\underline{P}^R|x_1' x_2'\rangle \\ &- \langle x_1|\underline{p}^R|x_1'\rangle\langle x_2|\underline{p}^R|x_2'\rangle + \tfrac{1}{2}\langle x_1|\underline{p}^R|x_2'\rangle\langle x_2|\underline{p}^R|x_1'\rangle] .\end{aligned}$$

The interesting feature of this equation is that it involves no terms linking two different groups. This is natural since the only correlation introduced in the strongly orthogonal group function approach is between electrons in the same group. In a general MC SCF wave function there will be correlation between groups, but I would expect these correlations to be weak. When the groups do not have $M_S = 0$, the exchange part of $\underline{P}$ is changed, but as long as most groups have $M_S = 0$, the decomposition of $\underline{P}$ in (5.3) should be reasonable.

It is a simple matter to derive the NO Hamiltonian with $\underline{P}$ decomposed as in Eq. (5.3). Let $\underline{\rho}$ now be constructed from the NO's rather than the NSO's. Define a Coulomb operator

$$\underline{J}_1[\underline{p}] = \mathrm{Tr}_2\, \underline{v}_{12}\, \underline{p}_2 \tag{5.6}$$

and an exchange operator

$$\langle x_1|\underline{K}[\underline{p}]|x_1'\rangle = |x_1 - x_1'|^{-1}\langle x_1|\underline{p}|x_1'\rangle . \tag{5.7}$$

I have assumed that

$$\langle x_1 x_2|\underline{v}_{12}|x_1' x_2'\rangle = |x_1 - x_2|^{-1}\delta(x_1 - x_1')\delta(x_2 - x_2').$$

The operators $\underline{J}$ and $\underline{K}$ are functionals of $\underline{p}$. Rewrite Eq. (4.7) in terms of these operators, and $\underline{\rho}$, $\underline{p}$, and $\underline{g}$.

$$\begin{aligned}(\underline{1} - \underline{\rho}_1)(\underline{h}_1 \underline{p}_1 + \underline{J}_1[\underline{p}]\underline{p}_1 - \tfrac{1}{2}\underline{K}_1[\underline{p}]\underline{p}_1 \\ + \mathrm{Tr}_2\, \underline{v}_{12}\underline{g}_{12})\underline{\rho}_1 = 0.\end{aligned} \tag{5.8}$$

The most tricky step in deriving (5.8) is to show that $\underline{K}[\underline{p}]$ really does come into it. Define $(\underline{p})^{-1}$ such that

$$(\underline{p})^{-1}\underline{p} = \underline{p}(\underline{p})^{-1} = \underline{\rho} \tag{5.9}$$

and

$$\underline{q}_1 = \mathrm{Tr}_2\, \underline{v}_{12}\, \underline{g}_{12} , \tag{5.10a}$$

$$\underline{G} = (\underline{1} - \underline{\rho})\underline{q}(\underline{p})^{-1} . \tag{5.10b}$$

Then multiply (5.8) from the right by $(\underline{p})^{-1}$.

$$(\underline{1} - \underline{\rho})\{\underline{h} + \underline{J}[\underline{p}] - \tfrac{1}{2}\underline{K}[\underline{p}] + \underline{G}\}\underline{\rho} = 0. \tag{5.11}$$

In this equation $\underline{G}$ is the only non-Hermitian operator. The operator in the curly brackets can be made Hermitian as in Sec. 4 by adding $\underline{G}^\dagger$ to $\underline{G}$. The operator $\underline{G}^\dagger$ can be added since $\underline{G}^\dagger\underline{\rho} = 0$. Thus if ψ_μ is an occupied NO, Eq. (5.11) says that

$$(\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K} + \underline{G} + \underline{G}^\dagger)\psi_\mu = \underline{\rho}(\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K})\underline{\rho}\psi_\mu . \tag{5.12}$$

This result is to be compared with Eq. (4.11). This is the first step in deriving what I believe to be the useful form of the NO Hamiltonian.

The second step is to define $\underline{N}$, the operator which guarantees that the ψ_μ are NO's. First rewrite Eq. (4.3) in terms of the spinless operators.

$$\underline{\rho}[\underline{p}(\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K}) - (\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K})\underline{p} + \underline{q}^\dagger - \underline{q}]\underline{\rho} = 0. \tag{5.13}$$

Let p_μ be the occupation number of ψ_μ, and assume that $p_\mu = p_\nu$ for $\mu \neq \nu$ only when it is required by the symmetry of the system. (See II for a detailed discussion.) Define for $\mu \neq \nu$ and $p_\mu \neq p_\nu$, the operator $\underline{N}$ in the space of the occupied NO's by its matrix elements

$$\langle\psi_\mu|\underline{N}|\psi_\nu\rangle = (p_\mu - p_\nu)^{-1}\langle\psi_\mu|\underline{q}^\dagger - \underline{q}|\psi_\nu\rangle, \tag{5.14a}$$

$$\underline{N} = \sum_{\substack{\mu\neq\nu \\ (p_\mu\neq p_\nu)}}^{\mathrm{occ}}\sum |\psi_\mu\rangle\langle\psi_\mu|\underline{N}|\psi_\nu\rangle\langle\psi_\nu| . \tag{5.14b}$$

Then if the NO's are chosen to be eigenfunctions of the operator $\underline{\rho}(\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K} + \underline{N})\underline{\rho}$, Eq. (5.13) will be satisfied.

$$\underline{\rho}(\underline{h} + \underline{J} - \tfrac{1}{2}\underline{K} + \underline{N})\underline{\rho}\psi_\mu = \epsilon_\mu\psi_\mu . \tag{5.15}$$

I can combine Eqs. (5.13) and (5.15) in the same way and for the same reasons that I combined Eqs. (4.5) and (4.11). Define

$$\underline{F} = \underline{h} + \underline{J} - \tfrac{1}{2}\underline{K} + \underline{N} + \underline{G} + \underline{G}^\dagger . \tag{5.16a}$$

This is the NO Hamiltonian. The NO eigenvalue equation is

$$\underline{F}\psi_\mu = \epsilon_\mu\psi_\mu . \tag{5.16b}$$

The eigenvalue ϵ_μ of Eq. (5.16b) includes directly the interaction of an electron in the orbital ψ_μ with the rest of the electrons in the system since

$\langle\psi_\mu|\underline{J}|\psi_\mu\rangle \neq 0$, and $\langle\psi_\mu|\underline{K}|\psi_\mu\rangle \neq 0$.

The eigenvalue in Eq. (4.12b) is equal to $\langle\psi_\mu|h|\psi_\mu\rangle$ and thus includes electronic interactions only indirectly. For this reason I believe that the eigenvalue of Eq. (5.16b) is more likely to have physical significance than that of Eq. (4.12b).

At the beginning of this section I said that it would be useful to reduce the contribution of N and $\underline{G}$ to the final equation. The explicit introduction of Coulomb and exchange contributions to $\underline{P}_{12}$ accomplishes this, for now $\underline{N}$ and $\underline{G}$ depend only upon the correlation function $\underline{g}_{12}$, rather than the whole two-body density matrix.[31] That it should be advantageous to include the Coulomb and exchange terms explicitly is supported by the properties of strongly orthogonal group functions and Hartree-Fock functions. That this causes the ϵ_μ to depend explicitly on the one-body density matrix through Coulomb and exchange operators I believe is an advantage.

6. SOLVING THE NATURAL-ORBITAL EQUATION

The solution of the NO equation given in Sec. 5 is not easy, but it is also not impossible. The difficulties are for the most part common to MC SCF theories. There are also simplifying aspects to the problem which should be recognized in programming the theory. (We are currently debugging such a program here.) It is to the difficulties and simplifications implicit in MC SCF theory that this section is devoted. The simplifications are discussed first.

One simplification of the programming and the computing offered by the NO equation, is that all of the NO's are eigenfunctions of the same one-electron Hamiltonian. This is a simplification in two ways. Firstly, there is only one effective Hamiltonian to be constructed. Secondly, because the NO's are all eigenfunctions of the same Hamiltonian, the ambiguity as to which eigenfunctions of which Hamiltonian are occupied[32] is reduced. The ambiguity as to which eigenfunctions of the Hamiltonian are occupied is not completely removed in my formulation of MC SCF theory, for the same reason that there can be ambiguities in even the closed-shell Hartree-Fock theory. This is essentially a question of the stability of SCF states.[33–34] I have derived a compact expression for the stability condition on MC SCF wave functions,[35] but unfortunately it has not yet suggested criteria for choosing the occupied orbitals.

Another simplification implicit in the MC SCF formalism I have given, is more a recognition that the operators used do not require that a large amount of new information be put into the program or into the data set. At first the need to construct one- and two-body density matrices suggests that new, complex information must be supplied to carry out a computation. In fact, this is not the case. The information needed to construct the density matrices is the same as that needed to do the configuration-interaction part of the calculation. The programs which are being written at Rutgers take advantage of this.

The complexity in the application of MC SCF theory lies in the coupling of two SCF procedures. Self-consistency must be reached in both the NO's and in the coefficients of the Slater determinants. The easiest way to describe the computational procedure is in terms of a flow chart (Fig. 1). The over-all procedure has been called a grand iteration procedure by Das and Wahl.[11]

The procedure outlined in Fig. 1 differs from theirs in that steps III and IV are not required in their case. This is due to the restrictions they place on the kinds of configurations which are allowed to interact. In any restricted MC SCF theory in which the starting orbitals are automatically NO's, steps III and IV are unnecessary. Step IV is unnecessary also when the MC wave function is constructed from all of the *N*-electron Slater determinants which can be constructed from *M* occupied orbitals. In general, however, step III will yield NO's different from the starting NO's, so that if only a selected set of configurations are allowed to interact, the CI wave function will depend upon the NO's used, even though two different sets of NO's span the same part of the one-electron Hilbert space. The other steps must be included in all MC SCF calculations.

The most important practical question is, will an SCF procedure based on Eq. (5.16) converge? At present it is well known that the computer programs based on other forms of MC SCF theory have convergence problems, so I expect that our program will have the same problems. It is straightforward to demonstrate however that all the convergence difficulties lie in finding SCF solutions to equations like (5.16) with fixed CI coefficients. Once such a solution is obtained, redetermining the CI coefficients must lower the energy, i.e., this step is convergent. The basic practical problem then, is to find a convergent procedure for solving Eq. (5.16). It is possible that this procedure may consist of solving some of the equations that led to Eq. (5.16), rather than that equation.

In Paper II, I discussed briefly the possibility that the $\underline{F}$ defined there would be dominated by $\underline{N}$ due to the latter containing $(p_\mu - p_\nu)^{-1}$. The $\underline{F}$ defined in Eq. (5.16a) might be dominated by $\underline{G}$ as well, since $\underline{G}$ depends on $p_\mu{}^{-1}$. I have constructed $\underline{F}$ for an infinite system in the alternant molecular orbital case, and I have found that neither $\underline{G}$ nor $\underline{N}$ dominates $\underline{F}$. On the other hand in the debugging of our MC SCF computer program

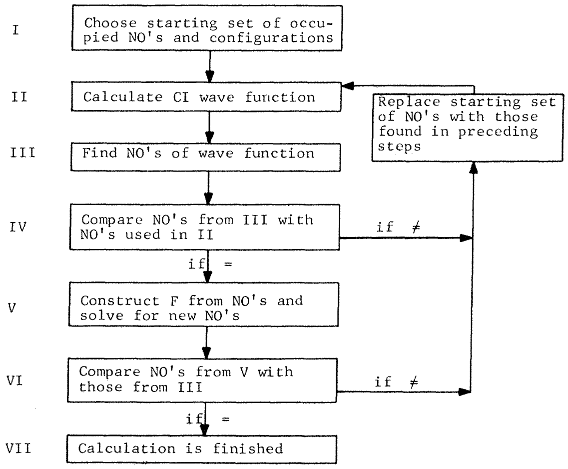

FIG. 1. Steps in the grand iteration procedure of MC SCF theory.

I have seen some examples in which $\underline{N}$ was dominant, but this could have been caused by errors in the program or by poor choices of the starting orbitals. Only experience can show in this case what the general situation is.

The application of the MC SCF formalism I have developed requires a considerable programming effort as should be expected. However, the SCF equation derived here is valid for most restricted MC SCF methods including those for which SCF equations have not been given previously, e.g., the alternant molecular orbital method.[26] Thus the subroutines that construct the operators $\underline{J}$, $\underline{K}$, $\underline{N}$, $\underline{G}$, and $\underline{F}$ might be written so that they use $\underline{p}_1$ and $\underline{P}_{12}$. Which method is used in a given calculation would be determined entirely by the rules used to construct $\underline{p}_1$ and $\underline{P}_{12}$, and by the way the C_K are determined.

7. CONCLUSION

In essence Eq. (5.16b) with the $\underline{F}$ defined in Eq. (5.16a), is a master equation for MC SCF theory. The equation is valid for any MC SCF theory in which it is convenient to solve for natural orbitals. In Sec. 2 I indicated that in nearly all of the restricted MC SCF theories so far suggested, NO's can play such a central role.

ACKNOWLEDGMENTS

I thank the Argonne National Laboratory for appointment as a Visiting Scientist during the summers of 1966 and 1967. I am particularly grateful to Dr. G. L. Goodman and Dr. A. C. Wahl for the hospitality I enjoyed there.

---

[*] Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[†] Permanent address:

[1] W. H. Adams, preceding paper Phys. Rev. 182, (1968).

[2] W. H. Adams, Phys. Rev. 156, 109 (1967).

[3] W. H. Adams, J. Chem. Phys. 37, 2009 (1962).

[4] J. Frenkel, Wave Mechanics, Advanced General Theory (Clarendon Press, Oxford, England, 1934), pp. 460–462.

[5] J. C. Slater, Phys. Rev. 91, 528 (1953).

[6] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

[7] R. McWeeny, Proc. Roy. Soc. (London) A232, 114 (1955).

[8] (a) T. L. Gilbert, J. Chem. Phys. 43, S248 (1965); (b) M. L. Benston and D. P. Chong, Mol. Phys. 14, 449 (1968).

[9] C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960); C. C. J. Roothaan and P. S. Bagus, Methods in Computational Physics (Academic Press Inc., New York, 1963), Vol. II, p. 47.

[10] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. (London) A238, 229 (1939).

[11] G. Das and A. C. Wahl, J. Chem. Phys. 44, 87 (1966); 47, 2923 (1967). G. Das, J. Chem. Phys. 46, 1568 (1967).

[12] A. Veillard, Theoret. Chim. Acta 4, 22 (1966); A. Veillard and E. Clementi, *ibid.* 7, 133 (1967); E. Clementi and A. Veillard J. Chem. Phys. 44, 3050 (1960).

[13] C. Froese, Proc. Phys. Soc. (London) 90, 39 (1967).

[14] J. Hinze and C. C. J. Roothaan, Progr. Theoret. Phys. (Kyoto) 40, 37 (1967).

[15] A. P. Yutsis, Zh. Eksperim. i Teor. Fiz. 23, 129 (1952). A useful review and guide to the work of Yutsis and co-workers has been given by A. P. Yutsis, Ya. I. Vizbaraite, T. D. Strotskite, and A. A. Bandzaites, Opt. i Spektroskopiya 12, 157 (1962) [English transl.: Opt. Spectry. (USSR) 12, 83 (1962)].

[16] A. C. Hurley, J. E. Lennard-Jones, and J. P. Pople, Proc. Roy. Soc. (London) A220, 446 (1953).

[17] T. Arai, J. Chem. Phys. 33, 95 (1960). A generalization of this result to McWeeny's group functions (see Ref. 18) was given by P. O. Löwdin, *ibid.* 35, 78 (1961).

[18] W. Kutzelnigg, J. Chem. Phys. 40, 3640 (1964).; R. Ahlrichs and W. Kutzelnigg, *ibid.* 48, 1819 (1968).

[19] (a) R. G. Parr, F. O. Ellison, and P. G. Lykos, J. Chem. Phys. 24, 1106 (1956); (b) R. McWeeny, Proc. Roy. Soc. (London) A253, 242 (1959); Rev. Mod. Phys. 32, 335 (1960).

[20] M. Klessinger and R. McWeeny, J. Chem. Phys. 42, 3343 (1965).

[21] R. McWeeny and E. Steiner, Advan. Quantum Chem. **2**, 93 (1965).

[22] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955); Ann. Acad. Reg. Sci. Upsaliensis **2**, 127 (1958).

[23] (a) M. Kotani, *Calcul des Fonctions d'Onde Moléculaire*, edited by R. Daudel (Centre National de Recherche Scientifique, Paris, 1958), pp. 39–46; (b) W. A. Goddard, III, Phys. Rev. **157**, 73, 81 (1967); **168**, 120 (1968).

[24] J. E. Harriman, J. Chem. Phys. **40**, 2827 (1964).

[25] P. O. Löwdin, *Symposium on Molecular Physics* (Maruzen, Tokyo, Japan, 1953), p. 13.

[26] This work has been given a unified exposition by R. Pauncz, *Alternant Molecular Orbital Method* (W. B. Saunders Company, Philadelphia, Pa., 1967).

[27] C. Edmiston and M. Krauss, J. Chem. Phys. **45**, 1833 (1966).

[28] C. F. Bender and E. R. Davidson, J. Phys. Chem. **70**, 2675 (1967).

[29] H. Shull and P. O. Löwdin, Phys. Rev. **110**, 1466 (1958); P. O. Löwdin, Advan. Chem. Phys. **2**, (1959).

[30] E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930); J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933).

[31] In case anyone wonders about it, it is not possible to eliminate all the Coulomb and exchange type contributions to g_{12} without complicating $\underline{F}$ with other non-Hermitian operators like $\underline{G}$. One could, however, multiply both the Coulomb and exchange terms I have introduced, by arbitrary constants and adjust these so that $\underline{G}$ and $\underline{N}$ are less important. It is not obvious what criteria should be used to choose the constants different from unity. A second possibility is to redefine $\underline{J}$ and $\underline{K}$ as in Ref. 9.

[32] In open-shell Hartree-Fock theory as described in Ref. 9, some care must be taken in deciding which of the closed-shell and open-shell eigenfunctions are occupied. In the Li atom, for example, the open-shell equation gives a 1*s* orbital as well as a 2*s* orbital. This 1*s* orbital is not identical to the 1*s* orbital calculated with the closed-shell Hamiltonian. I thank Dr. Paul Bagus, Dr. A. C. Wahl, and Dr. W. Huo for discussions on this point.

[33] For an extensive discussion of the stability problem in the Hartree-Fock theory, see W. H. Adams, Phys. Rev. **127**, 1650 (1962).

[34] Some recent studies of the Hartree-Fock stability problem are T. A. Kaplan and W. H. Kleiner, Phys. Rev. **156**, (1967). J. Cizek and J. Paldus, J. Chem. Phys. **47**, 3976 (1967); R. E. Stanton, *ibid.* **48**, 257 (1968).

[35] W. H. Adams (unpublished).

PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Correlation Energies of Some States of 3-10 Electron Atoms

Robert E. Knight
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506

(Received 11 April 1969)

The nonrelativistic eigenvalues of several states of 3–10 electron atoms are calculated to second order in the nuclear charge Z. It is noted that with some modifications the Hylleraas variational procedure can be employed successfully for a many-electron atom.

I. INTRODUCTION

Conventional Schrödinger perturbation theory presents the energy and wave function of an atomic state, of arbitrary nuclear charge Z, as an expansion in the inverse powers of the nuclear charge. For any atomic state the zero-order wave function Ψ_0 and the first two perturbation coefficients ϵ_0 and ϵ_1 can be found exactly. The second-order coefficient ϵ_2 has been calculated for a number of atomic states using a variational perturbation technique due to Hylleraas.[1] Most of these calculations have been restricted to two-electron systems.[2] In order to extend the procedure to a many-electron atom, Chisholm and Dalgarno[3] have shown that the first-order wave function for a many-electron atom is naturally partitioned into two-electron pair functions. The purpose of this work is to show that the calculation of the first-order wave functions and second-order perturbation coefficients is practical for many-electron atoms.