Orbital Self-Consistent-Field Theory. I. General Theory for Multiconfigurational Wave Functions

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A general formulation of multiconfigurational self-consistent-field theory is given. The fundamental condition to be satisfied by the M occupied orbitals ψ_μ of an $N(\leq M)$-body system, in order that the total energy of one state be extremalized, is expressed in terms of the fundamental invariant $\varrho=\sum_{\mu=1}^{M}|\psi_\mu\rangle\langle\psi_\mu|$. The condition placed on ϱ is of the same form as the condition on the fundamental invariant of the Hartree-Fock theory. Setting $M=N$, we derive the unrestricted Hartree-Fock equations from the condition on ϱ. For $M>N$ there are three freedoms one may take with the fundamental condition on ϱ. Exploiting any or all of these freedoms yields alternative forms of the fundamental condition. This enables us to derive an effective one-body Hamiltonian which is the sum of a Hartree-type Hamiltonian and a correlation and exchange operator. For finite $M>N$, the one-body Hamiltonian contains a nonlocal exchange and correlation operator. This operator is defined in terms of the one- and two-body density matrices. The connection between the orbitals of this theory and those of the Hartree-Fock theory is explored. The theory as outlined here is applicable to any system of N identical particles, but our discussion is oriented towards electronic systems. The theory contains most self-consistent-field theories as special cases, and gives a basis for the self-consistent-field formulation of others.

1. INTRODUCTION

THE physically accurate approximation of the wave functions of N-body systems in a manner which is mathematically well defined and numerically tractable, and which at the same time lends itself to physical interpretation, has been an important problem for many years. One promising method is multiconfigurational self-consistent-field theory, as has been recognized by an increasing number of authors. It is this theory which is formulated and investigated here. The formulation we give bears a close resemblance to the Hartree-Fock self-consistent-field theory (single configuration), and in fact contains it and various approximations to multiconfigurational self-consistent-field theory, as special cases.

Multiconfigurational (MC) self-consistent-field (SCF) theory approximates the wave function of a system of N identical particles by a linear combination of N-body functions, which are products of N orbitals. The N orbitals in each product are selected from a set of $M\geqslant N$ orbitals. If M is finite, the energy of one state of the system may be extremalized with respect to the orbitals and the linear coefficients of the orbital products. This leads to an SCF equation for the orbitals and the linear coefficients. (If the orbitals form a complete set, only the linear coefficients need be varied to extremalize the energy.) Having determined a set of M orbitals in this way, the linear coefficients of the orbital products can be chosen also to yield upper bounds to the energies of other states of the system, as is well known.[1] Of course the approximate eigenvalues for these other states may not be as accurate as for the state with respect to which the orbitals were optimized.

The first general discussion of MC-SCF theory seems to be that of Frenkel.[2] He presented a second-quantized formulation of the theory. Later several other authors formulated the general theory without using second quantization.[3–5] Practical applications have been limited to two- to four-electron systems, apparently because of the inconvenient form of the equations. Still other authors have suggested or investigated versions of MC-SCF theory that have restrictions built into them, in order to simplify the application of the theory.[6–9] As with the general theory, applications of the restricted MC-SCF theories have been few in number. (There are a number of non-SCF calculations.) Since 1955 a number of authors have investigated MC-SCF theory from a variety of points of view, particularly with the object of putting it into a practical form. Reference to this later work will be made when it is most relevant to our discussion.

The interest in MC-SCF can be traced to several factors. An orbital theory of an N-body system offers a picture of that system, particularly when only a relatively small number of N-body orbital products have been linearly combined to form the wave function. Such wave functions at least hold the promise of

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[9] (a) P.-O. Löwdin, in Symposium on Molecular Physics, Nikko, Japan, 1954, p. 599 (unpublished); (b) Phys. Rev. **97**, 1509 (1955).

yielding a simple interpretation of elementary processes such as ionization. Furthermore a MC-SCF theory can introduce some of the important particle correlations which are omitted in the Hartree-Fock theory. For example for most molecules a MC-SCF theory for the electronic wave function is necessary to obtain the correct dissociation products.[10–12] In atoms, MC-SCF theory can introduce important angular correlations.[6,7,13,14] In practice a MC-SCF theory can be expected to yield much more accurate energies and charge distributions, as evidenced by the computations which have been carried out.[7,13–15]

The approach to MC-SCF theory that we have adopted has certain advantages over the previous general formulations. In particular our formulation emphasizes and takes advantage of the independence of the variational condition on the orbitals and the variational condition on the coefficients of the orbital products. (This independence was noted by Frenkel.[2]) The condition which the orbitals used in the MC-SCF theory must satisfy in order to extremalize the energy has the same form as the corresponding condition of the Hartree-Fock theory. This implies that localized orbital and pseudopotential methods[16–18] can be used in this generalized SCF theory. Also it opens the possibility of looking for orbitals in the MC-SCF approximation which are transferable from one system to another.[19,20] The generality of our formulation is such that it applies equally well to the orbitals of any restricted MC-SCF approximation,[8,9,21–24] i.e., to the orbitals of an approximation which uses in the wave function only a *wisely* chosen few of the N-electron determinants which might be constructed from $M>N$ orbitals, or which does not vary independently the coefficients of those determinants. In a restricted MC-SCF theory, however, the condition we give serves to define only the occupied and unoccupied subspaces, but not the individual occupied orbitals. The occupied orbitals must satisfy further conditions which arise from the requirement that the energy be extremalized with respect to the mixing together of occupied orbitals. These further conditions will be taken up in later papers dealing with specific restricted MC-SCF theories.

In the next section we derive the fundamental condition which determines the M orbitals of an MC-SCF wave function so that the energy of a state of an N-particle system is extremalized. (The theory is applicable to any system of N identical particles which interact via potentials which have no hard core. However we develop the theory herein with the object of applying it to electronic systems.) We present arguments to show that the fundamental condition on the orbitals, applies also to the restricted MC-SCF theories. In order to make the argument of Sec. 2 more obvious, we derive in Sec. 3 from the condition found in Sec. 2 the Hartree-Fock SCF theory for fermions. Section 4 shows how a condition equivalent to that of Sec. 2 may be derived by taking certain liberties with the original equations. In conjunction with this we relate the total energy to the orbital eigenvalues. Section 5 indicates how the orbitals of our theory may be related to those of the Hartree-Fock theory. The article closes with a discussion of some of the problems which remain to be solved.

2. THE FUNDAMENTAL CONDITION ON THE ORBITALS

The fundamental condition which the M occupied orbitals of a MC-SCF wave function for an N-electron system must satisfy in order to extremalize the energy can be derived in a straightforward fashion. This derivation has the advantage of emphasizing that the variation of the orbitals and the variation of the determinant coefficients are independent in the first order. This point has been made several times in the past[2,5] in connection with the general MC-SCF theory, but not in connection with some of the restricted theories.[8,9,21–24] Furthermore the generality of the formulation we give promises to aid us later in the understanding and application of MC-SCF theory.

The method we adopt in our derivation is to construct a projection operator $\mathbf{O}$ that will reproduce any N-body wave function Ψ which can be constructed from a set of M ($\geqslant N$) orthonormal spin orbitals ψ_μ, by forming a weighted sum of antisymmetrized products (Slater determinants) of N spin orbitals each. We require that the orbitals and Ψ be chosen to extremalize $\langle\Psi|\mathbf{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$, where $\mathbf{H}$ is the N-body Hamiltonian. There are alternatives to this choice,[25] but they do not seem to be practical alternatives. Furthermore our choice is favored by both the Eckart criterion[26] and the "separation theorem."[1] Specifying Ψ in this manner for a fixed set

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[24] T. L. Gilbert, J. Chem. Phys. **43**, S248 (1965).

[25] Alternative choices have been discussed extensively by W. Kutzelnigg and V. H. Smith, Quantum Chemistry Group, Uppsala, Sweden, Reports No. 130 and 138, 1964 (unpublished).
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of spin orbitals yields the equation

$$\mathbf{OHO}\Psi = E\Psi. \tag{2.1}$$

There are as many different eigenfunctions of **OHO** as there are different Slater determinants of the M orbitals. Equation (2.1) suggests how to include variations of the ψ_μ's.

When the ψ_μ's are varied, **O** will change, and also the effective Hamiltonian **OHO**. A first-order change in the ψ_μ then gives a first-order change in **OHO**. Accordingly the best set of spin orbitals are those which make the first-order correction to E vanish. We define

$$\mathfrak{H}\mathcal{C} = \mathbf{OHO} + (\mathbf{1}-\mathbf{O})\mathbf{H}(\mathbf{1}-\mathbf{O}). \tag{2.2a}$$

The addition of $(\mathbf{1}-\mathbf{O})\mathbf{H}(\mathbf{1}-\mathbf{O})$ to **OHO** is arbitrary, but attractive since it makes $\mathfrak{H}\mathcal{C}$ differ less from **H**. (Its presence is essential to the derivation of the theorem on perturbation corrections cited in Sec. 6 and to the investigation of a problem we shall consider in a later paper.) It has no effect on the wave function Ψ whose energy is extremalized, since $(\mathbf{1}-\mathbf{O})\Psi = 0$.

$$\mathfrak{H}\mathcal{C}\Psi = E\Psi. \tag{2.2b}$$

Let $\mathfrak{H}\mathcal{C}^{(1)}$ be the first-order correction to $\mathfrak{H}\mathcal{C}$ due to the variation of the ψ_μ's. The condition on the orbitals is simply

$$E^{(1)} = \langle \Psi | \mathfrak{H}\mathcal{C}^{(1)} | \Psi \rangle = 0. \tag{2.3}$$

It is from this expression that we obtain our fundamental condition on the orbitals, i.e., the condition for the orbitals to extremalize E.

The projection operator **O** is constructed straightforwardly from the *fundamental invariant*[27] of MC-SCF theory. The fundamental invariant in the coordinate (space and spin for one electron) representation, assuming the ψ_μ are orthonormalized, is

$$\langle x_i | \varrho_i{}^j | x_j \rangle = \sum_{\mu=1}^{M} \psi_\mu(x_i)\psi_\mu{}^*(x_j). \tag{2.4}$$

When $j = i'$ we shall write simply ϱ_i, it being understood to represent $\varrho_i{}^{i'}$. The fundamental invariant is a projection operator, i.e.,

$$\int dx_j \langle x_i | \varrho_i{}^j | x_j \rangle \langle x_j | \varrho_j{}^{i'} | x_i' \rangle = \langle x_i | \varrho_i{}^{i'} | x_i' \rangle,$$

or, in the shorthand we use (transformation theory conventions),

$$\varrho_i \varrho_i = \varrho_i.$$

If the ψ_μ's are not orthogonal, they must be linearly independent, so that one can construct ϱ_i from them.[28]

[27] This is an obvious extension of the viewpoint and nomenclature used by P.-O. Löwdin in Ref. 9(b).

[28] This is the same as constructing the fundamental invariant of the Hartree-Fock theory from a nonorthogonal set of orbitals. See W. H. Adams, J. Chem. Phys. 34, 89 (1961).

The desired projection operator **O**, as may be readily verified, is

$$\mathbf{O} = \prod_{i=1}^{N} \varrho_i. \tag{2.5}$$

(It is not necessary to make **O** symmetric or antisymmetric under the interchange of pairs of coordinates as long as the wave function Ψ is made to have the correct permutational symmetry.) Since $\langle x_i | \varrho_i | x_i' \rangle$ is invariant under nonsingular, linear transformations of the ψ_μ, so is **O**.

The allowed first variation of **O** must be derivable from the first variation of the fundamental invariant, if the variations are to be consistent with a wave function constructed as a sum of Slater determinants. The variation of the fundamental invariant such that its idempotency is maintained can be carried out in the same manner as in the Hartree-Fock theory.[29] Let $\langle x_i | \mathbf{\Delta}_i | x_i' \rangle$ be any function of x_i and x_i'.
Define

$$\mathbf{u}_i = (\mathbf{1}-\varrho_i)\mathbf{\Delta}_i\varrho_i. \tag{2.6}$$

The first variation of ϱ_i is (λ is the small number which defines the order of the variation)

$$\delta\varrho_i = \lambda\varrho_i{}^{(1)} = \lambda(\mathbf{u}_i + \mathbf{u}_i{}^\dagger). \tag{2.7}$$

The first variation $\delta\mathbf{O}$ of **O** should be of the first order in λ, so that

$$\delta\mathbf{O} = \lambda \sum_{i=1}^{N} \varrho_i{}^{(1)} \prod_{j\neq i}^{N} \varrho_j. \tag{2.8}$$

For our purposes it will be useful to have $\delta\mathbf{O}$ expressed in terms of $\mathbf{\Delta}_i$.

$$\delta\mathbf{O} = \lambda \sum_{i=1}^{N} \{(\mathbf{1}-\varrho_i)\mathbf{\Delta}_i\mathbf{O} + \mathbf{O}\mathbf{\Delta}_i{}^\dagger(\mathbf{1}-\varrho_i)\}. \tag{2.9}$$

Using this expression for $\delta\mathbf{O}$, we can construct $\mathfrak{H}\mathcal{C}^{(1)}$ and $E^{(1)}$.

From Eqs. (2.2) it follows that

$$\mathfrak{H}\mathcal{C}^{(1)} = \mathbf{OH}\delta\mathbf{O} + \delta\mathbf{OHO} - (\mathbf{1}-\mathbf{O})\mathbf{H}\delta\mathbf{O} - \delta\mathbf{OH}(\mathbf{1}-\mathbf{O}). \tag{2.10}$$

Since $(\mathbf{1}-\mathbf{O})\Psi = 0$, the expression for $E^{(1)}$ is just

$$E^{(1)} = \langle \Psi | \mathbf{OH}\delta\mathbf{O} + \delta\mathbf{OHO} | \Psi \rangle. \tag{2.11}$$

We assume that **H** can be written as a sum of one-electron operators $\mathbf{h}_i$ which operate only on the ith coordinate, and two-electron operators $\mathbf{v}_{ij} = \mathbf{v}_{ji}$, which operate only on the ith and jth electron coordinates.

$$\mathbf{H} = \sum_{i=1}^{N} \mathbf{h}_i + \tfrac{1}{2} \sum_{i\neq j}^{N}\sum \mathbf{v}_{ij}. \tag{2.12}$$

Combining Eqs. (2.9), (2.11), and (2.12), and noting

[29] R. McWeeny, Rev. Mod. Phys. 32, 335 (1960), Eqs. (74) and (75).

that $(\mathbf{1}-\boldsymbol{\varrho}_i)\Psi=0$ and $\mathbf{O}\Psi=\Psi$, we can write

$$E^{(1)}=\lambda\langle\Psi|\sum_{i=1}^{N}[\boldsymbol{\varrho}_i\mathbf{h}_i(\mathbf{1}-\boldsymbol{\varrho}_i)\boldsymbol{\Delta}_i+\boldsymbol{\Delta}_i^\dagger(\mathbf{1}-\boldsymbol{\varrho}_i)\mathbf{h}_i\boldsymbol{\varrho}_i]$$
$$+\sum_{i\neq j}\sum\boldsymbol{\varrho}_i\boldsymbol{\varrho}_j[\mathbf{v}_{ij}(\mathbf{1}-\boldsymbol{\varrho}_i)\boldsymbol{\Delta}_i$$
$$+\boldsymbol{\Delta}_i^\dagger(\mathbf{1}-\boldsymbol{\varrho}_i)\mathbf{v}_{ij}]\boldsymbol{\varrho}_i\boldsymbol{\varrho}_j|\Psi\rangle. \quad (2.13)$$

We can make $E^{(1)}$ look simpler by writing it in terms of reduced density matrices.[4] We normalize the one-electron density matrix $\boldsymbol{\gamma}_i=\boldsymbol{\gamma}_i{}^{i'}$ to N (the subscript and superscript refer to the ith coordinate), the two-electron density matrix $\boldsymbol{\Gamma}_{ij}=\boldsymbol{\Gamma}_{ij}{}^{i'j'}$ to $N(N-1)$.[21] (The subscripts and superscripts refer to the ith and jth coordinates.) To indicate that the trace over all indices is formed, we write Tr in front of the equation for $E^{(1)}$.

$$E^{(1)}=\lambda\ \mathrm{Tr}\{\boldsymbol{\varrho}_1[\mathbf{h}_1(\mathbf{1}-\boldsymbol{\varrho}_1)\boldsymbol{\Delta}_1+\boldsymbol{\Delta}_1^\dagger(\mathbf{1}-\boldsymbol{\varrho}_1)\mathbf{h}_1]\boldsymbol{\varrho}_1\boldsymbol{\gamma}_1$$
$$+\boldsymbol{\varrho}_1\boldsymbol{\varrho}_2[\mathbf{v}_{12}(\mathbf{1}-\boldsymbol{\varrho}_1)\boldsymbol{\Delta}_1$$
$$+\boldsymbol{\Delta}_1^\dagger(\mathbf{1}-\boldsymbol{\varrho}_1)\mathbf{v}_{12}]\boldsymbol{\varrho}_1\boldsymbol{\varrho}_2\boldsymbol{\Gamma}_{12}\}. \quad (2.14)$$

The first variation $E^{(1)}$ must vanish for arbitrary $\boldsymbol{\Delta}_1$, if the M spin orbitals ψ_μ extremalize the energy. Note that $\boldsymbol{\varrho}_1\boldsymbol{\gamma}_1=\boldsymbol{\gamma}_1$ and $\boldsymbol{\varrho}_1\boldsymbol{\Gamma}_{12}=\boldsymbol{\varrho}_2\boldsymbol{\Gamma}_{12}=\boldsymbol{\Gamma}_{12}$. Let Tr_2 indicate that the trace is formed only over index 2. The fundamental condition is

$$(\mathbf{1}-\boldsymbol{\varrho}_1)[\mathbf{h}_1\boldsymbol{\gamma}_1+\mathrm{Tr}_2(\mathbf{v}_{12}\boldsymbol{\Gamma}_{12})]\boldsymbol{\varrho}_1=0. \quad (2.15)$$

It is a condition on $\boldsymbol{\varrho}_1$. Supplemented by the requirement that $\boldsymbol{\varrho}_1$ have trace M, and that it be Hermitian and idempotent, Eq. (2.15) determines $\boldsymbol{\varrho}_1$.[30,31] The equation has the same form as the fundamental condition of the Hartree-Fock theory.[31] In both cases $\boldsymbol{\varrho}_1$ is uniquely determined by the fundamental conditions. The M occupied orbitals are not uniquely determined without introducing some further condition.

The condition given by Eq. (2.15) applies when the coefficients of the determinantal functions in the MC wave function are fixed and when they are varied, when all determinants that can be constructed from the M occupied orbitals have been used in the wave function, and when only some of the possible determinants have been used. If the coefficients of the determinants are varied, e.g., when they are solutions of the secular equation for the N-electron problem, the orbitals determined by Eq. (2.15) with the initial choice of coefficients determine a new set of coefficients. The new orbitals and coefficients determine new density matrices which in turn determine a new set of orbitals, and so on, until self-consistency is achieved. When all possible N-electron determinant functions constructable from the M occupied orbitals are used in the MC wave function and when self-consistency is achieved between the orbitals and determinant coefficients, then E, $\boldsymbol{\gamma}_1$, and $\boldsymbol{\Gamma}_{12}$ will be determined by $\boldsymbol{\varrho}_1$ in a certain sense. They will be determined by $\boldsymbol{\varrho}_1$ so long as it is understood that for any choices of the M orbitals yielding the same $\boldsymbol{\varrho}_1$, a corresponding set of determinant coefficients exists which will give the same E, $\boldsymbol{\gamma}_1$, and $\boldsymbol{\Gamma}_{12}$. That this must be the case is obvious from the definition of $\mathfrak{H}$ and Eq. (2.2b). If only a selected set of the determinants constructable from the M orbitals is used in the wave function, then E, $\boldsymbol{\gamma}_1$, and $\boldsymbol{\Gamma}_{12}$ will depend upon the orbitals, not just on $\boldsymbol{\varrho}_1$. In this case Eq. (2.15) and the conditions on $\boldsymbol{\varrho}_1$ must be supplemented by a condition which will make the energy stationary with respect to variations which mix the occupied orbitals. That Eq. (2.15) places a condition on the orbitals of any MC theory is a consequence of the linear independency of the three first-order variations, namely, the variation which mixes configurations, the variation which mixes occupied orbitals among themselves, and the variation which mixes occupied orbitals with virtual orbitals. Equation (2.15) arises from the third variation. It is straightforward to show that Eq. (2.15) is equivalent to the equations found by Löwdin[3] and McWeeny.[4] In other cases the relationship between our Eq. (2.15) and those derived by other authors can be difficult to show. This is the case, for example, in relating Gilbert's recent theory[24] to ours. Nevertheless, since Gilbert's MC wave function can be reproduced by an operator $\mathbf{O}$, and since Gilbert minimizes the energy with respect to the orbitals, it is apparent that his orbitals must satisfy Eq. (2.15), and that from Eq. (2.15) we should be able to derive an equation related to his Eqs. (8) and (9). Although the relating of the two equations is not a straightforward exercise, we do not feel that it is an exercise worth including in this paper.

3. UNRESTRICTED HARTREE-FOCK THEORY

The familiar unrestricted and closed-shell Hartree-Fock theories can be derived from Eq. (2.15). This is a useful exercise for two reasons. Firstly, it connects the considerations of the preceding section with more familiar equations. Secondly, it emphasizes the basic condition of the Hartree-Fock theory, putting us in a better position to link the Hartree-Fock theory with the equations we advance in the next section. Our derivation is for fermions.

In the unrestricted Hartree-Fock (HF) theory $M=N$, and $\boldsymbol{\varrho}_i$ is the one-electron (Fock-Dirac) density matrix. The one- and two-electron density matrices are, respectively,

$$\boldsymbol{\gamma}_i=\boldsymbol{\varrho}_i, \quad (3.1)$$

$$\boldsymbol{\Gamma}_{ij}{}^{i'j'}=\boldsymbol{\varrho}_i{}^{i'}\boldsymbol{\varrho}_j{}^{j'}-\boldsymbol{\varrho}_i{}^{j'}\boldsymbol{\varrho}_j{}^{i'}. \quad (3.2)$$

A simplification in the appearance of Eq. (2.15) can be effected if we assume that

$$\langle x_ix_j|\mathbf{v}_{ij}|x_i'x_j'\rangle=v_{ij}\delta(x_i-x_i')\delta(x_j-x_j')$$

[30] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).
[31] W. H. Adams, Phys. Rev. **127**, 1650 (1962), Eq. (16).

(where v_{ij} is a function of x_i and x_j) and define

$$\langle x_i|\mathbf{B}_i|x_i'\rangle=\delta(x_i-x_i')\int v_{ij}\langle x_j|\varrho_j|x_j\rangle dx_j, \quad (3.3)$$

$$\langle x_i|\mathbf{A}_i|x_i'\rangle=v_{ii'}\langle x_i|\varrho_i|x_i'\rangle. \quad (3.4)$$

Substituting these operators in Eq. (2.15) we have

$$(1-\varrho_1)[\mathbf{h}_1\varrho_1+\mathbf{B}_1\varrho_1-\mathbf{A}_1\varrho_1]\varrho_1=0$$

or, factoring out ϱ_1 and defining

$$\mathbf{F}_1^{\mathrm{HF}}=\mathbf{h}_1+\mathbf{B}_1-\mathbf{A}_1 \quad (3.5)$$

(the one-electron Hamiltonian of the HF theory)

$$(1-\varrho_1)\mathbf{F}_1^{\mathrm{HF}}\varrho_1=0. \quad (3.6)$$

This is the fundamental condition of the unrestricted HF theory.[30,31] It also applies to the closed-shell, restricted HF theory.

The canonical HF equations may be derived from Eq. (3.6) by observing that

$$\varrho_1\psi_\mu(x_1)=\psi_\mu(x_1) \quad (3.7)$$

and

$$\mathbf{F}_1^{\mathrm{HF}}\psi_\mu(x_1)=\mathbf{F}_1^{\mathrm{HF}}\varrho_1\psi_\mu(x_1)=\varrho_1\mathbf{F}_1^{\mathrm{HF}}\varrho_1\psi_\mu(x_1). \quad (3.8)$$

In words, $\mathbf{F}_1^{\mathrm{HF}}$ applied to $\psi_\mu(x_1)$ yields a linear combination of the orbitals $\psi_1, \psi_2, \cdots, \psi_N$. We can choose the orbitals to be eigenfunctions of $\mathbf{F}_1^{\mathrm{HF}}$ since $\mathbf{F}_1^{\mathrm{HF}}$ is Hermitian, and since $\langle x_i|\varrho_i|x_i'\rangle$ and the single determinant wave function are invariant under unitary transformations of the orbitals.

$$\mathbf{F}_1^{\mathrm{HF}}\psi_\mu(x_1)=\epsilon_\mu^{\mathrm{HF}}\psi_\mu(x_1). \quad (3.9)$$

Thus we arrive at the eigenvalue equation of the unrestricted HF theory. The equation of the restricted theory for closed-shell systems may be derived from it, of course.

4. HARTREE THEORY WITH EXCHANGE AND CORRELATION

We have shown that the fundamental condition [Eq. (2.15)] on the M orbitals to be used in constructing an MC-SCF wave function has the form $(1-\varrho_1)\mathfrak{F}_1\varrho_1=0$, where $\mathfrak{F}_1=\mathbf{h}_1\gamma_1+\mathrm{Tr}_2(\mathbf{v}_{12}\Gamma_{12})$. This condition involves ϱ_1 and $1-\varrho_1$ in the same way that the fundamental condition of the HF theory [Eq. (3.6)] involves the corresponding ϱ_1 and $1-\varrho_1$. However, $\mathfrak{F}_1$ differs from the HF Hamiltonian in several ways. The question is then how significant are the differences. Or, to put it another way, can we replace the condition given by Eq. (2.15) by a mathematically equivalent condition involving an operator which differs less from the HF Hamiltonian? The answer is yes. There are three liberties that may be taken with Eq. (2.15). Two of these liberties will be taken in this section. The third, a liberty one may also take in the HF theory,[16,17] is explored in Sec. 5.

That it is possible to modify Eq. (2.15) without altering its mathematical content is important to know, whether or not one has reason for wanting to modify the equation. We feel that there are reasons for modifying the equation. For one thing the operator $\mathfrak{F}_1$ has nonzero eigenvalues only for the M occupied orbitals. We feel that this may prevent our inventing a physical interpretation for the orbitals and their eigenvalues. The explanation for this property of $\mathfrak{F}_1$ is that its eigenvalues must correspond to energies multiplied by occupation numbers. (This is exactly the case if $\mathbf{v}_{12}$ vanishes.) A practical reason for modifying $\mathfrak{F}_{12}$ so that it will differ less from the HF Hamiltonian is that in this way the N occupied HF orbitals will be better approximations to N of the M occupied orbitals of MC-SCF theory. Furthermore the observed differences between the occupied HF orbitals and the N corresponding MC-SCF orbitals will then be due only to essential differences in the effective Hamiltonians. This should be an advantage in trying to understand MC-SCF theory. A second practical reason for modifying $\mathfrak{F}_1$ is to get an operator which depends less strongly on the orbitals and the coefficients of the determinants, so that small changes in the orbitals and the coefficients will yield still smaller changes in the next iteration of the SCF calculation.

The two liberties that we take with Eq. (2.15) in this section will replace $\mathfrak{F}_1$ by an operator which more closely resembles the HF Hamiltonian. One liberty we take is to multiply Eq. (2.15) from the right by an operator which commutes with ϱ_1. The second liberty involves breaking Γ_{12} into two physically meaningful parts. In this way the resulting effective Hamiltonian is made to contain a Coulombic operator which is a functional of the one-body density matrix.

The operators $\mathfrak{F}_1$ and $\mathbf{F}_1^{\mathrm{HF}}$ differ in each term. In particular $\mathfrak{F}_1$ contains $\mathbf{h}_1\gamma_1$ while $\mathbf{F}_1^{\mathrm{HF}}$ contains only $\mathbf{h}_1$. However γ_1 and ϱ_1 commute, so that γ_1 may be factored out of the term in Eq. (2.15). Alternatively we can define an "inverse" to γ_1 in the sense that

$$(\gamma_1)^{-1}\gamma_1=\gamma_1(\gamma_1)^{-1}=\varrho_1. \quad (4.1)$$

The operator $(\gamma_1)^{-1}$ commutes with ϱ_1. (It will exist if the natural spin orbitals span the same space as the M orbitals ψ_μ.[32] If they do not, then some of the ψ_μ may be eliminated without changing the wave function.) Multiplying Eq. (2.15) from the right by $(\gamma_1)^{-1}$ will have the same effect on the $\mathbf{h}_1\gamma_1$ term as factoring out γ_1. Multiplying $\mathrm{Tr}_2(\mathbf{v}_{12}\Gamma_{12})$ from the right by $(\gamma_1)^{-1}$ will yield a non-Hermitian operator which is just as complicated as the original operator. However, we can take a liberty with Γ_{12} that will make at least part of $\mathrm{Tr}_2(\mathbf{v}_{12}\Gamma_{12})(\gamma_1)^{-1}$ have an obvious physical meaning.

The liberty we wish to take with Γ_{12} is to explicitly

[32] This statement is based on the results of Ref. 4, in particular Eq. (63).

divide it into an uncorrelated and a correlated part. If there were no correlations between the electrons, the two-electron density matrix would be $\gamma_1\gamma_2$. If we subtract $\gamma_1\gamma_2$ from Γ_{12}, we are left with a term which by definition contains all of the correlations between the electrons. Let us define

$$\mathbf{g}_{12}=\mathbf{\Gamma}_{12}-\gamma_1\gamma_2. \tag{4.2}$$

We could have also subtracted from Γ_{12} an exchange term of the form $\gamma_1{}^{2'}\gamma_2{}^{1'}$. While this form is correct for the exchange part of Γ_{12} in the unrestricted HF case, in the restricted HF case it is correct only when we are dealing with single determinant wave functions. For this reason we feel that at this point it is best not to separate the correlation operator $\mathbf{g}_{12}$ into a statistical and a dynamical part. Upon substitution for Γ_{12} we have

$$\mathrm{Tr}_2(\mathbf{v}_{12}\mathbf{\Gamma}_{12})(\gamma_1)^{-1}=\mathrm{Tr}_2[\mathbf{v}_{12}\varrho_1\gamma_2+\mathbf{v}_{12}\mathbf{g}_{12}(\gamma_1)^{-1}]. \tag{4.3}$$

Obviously the decomposition of Γ_{12} we have chosen is arbitrary, although it has a certain intuitive appeal.

The two liberties described above, which are to be taken with Eq. (2.15), yield

$$(\mathbf{1}-\varrho_1)[\mathbf{h}_1\varrho_1+\mathrm{Tr}_2(\mathbf{v}_{12}\gamma_2)\varrho_1 +\mathrm{Tr}_2(\mathbf{v}_{12}\mathbf{g}_{12}(\gamma_1)^{-1})]\varrho_1=0. \tag{4.4}$$

We can factor ϱ_1 out of the first two terms of the sum since $(\varrho_1)^2=\varrho_1$. The third term cannot be further simplified at this stage of our analysis, so we give to it a symbol, or rather to its product with $\mathbf{1}-\varrho_1$.

$$\mathbf{G}_1=(\mathbf{1}-\varrho_1)\,\mathrm{Tr}_2[\mathbf{v}_{12}\mathbf{g}_{12}(\gamma_1)^{-1}]. \tag{4.5}$$

Whether or not the factor of $\mathbf{1}-\varrho_1$ is included in $\mathbf{G}_1$, is a matter of taste at this time. (If it is left out, the expression given below for the total energy will have to be modified.) With $\mathbf{G}_1$ defined as in Eq. (4.5), the matrix element of $\mathbf{G}_1$ between any occupied orbitals will be zero. We define the Hermitian operator

$$\mathbf{F}_1=\mathbf{h}_1+\mathrm{Tr}_2(\mathbf{v}_{12}\gamma_2)+\mathbf{G}_1+\mathbf{G}_1{}^\dagger. \tag{4.6}$$

The equation

$$(\mathbf{1}-\varrho_1)\mathbf{F}_1\varrho_1=0 \tag{4.7}$$

is equivalent to Eq. (4.4) since $(\mathbf{1}-\varrho_1)\mathbf{G}_1{}^\dagger\varrho_1=0$. The operator $\mathbf{F}_1$ is the effective one-electron Hamiltonian we set out to find. The nonlocal operator $\mathbf{G}_1+\mathbf{G}_1{}^\dagger$ brings in the effects of both the statistical (exchange) and the dynamical correlations.

The operator $\mathbf{F}_1$ is quite similar to $\mathbf{F}_1{}^{\mathrm{HF}}$ [Eq. (3.5)]. The same one-electron operator $\mathbf{h}_1$ appears in both. The electronic Coulomb potential operator occurs in both. (The electronic density found with γ_1 and with the Fock-Dirac density matrix are not the same, of course.) The big difference between $\mathbf{F}_1$ and $\mathbf{F}_1{}^{\mathrm{HF}}$ lies in the nonlocal potentials. The nonlocal exchange potential of the HF operator is replaced by a nonlocal exchange and correlation potential $\mathbf{G}_1+\mathbf{G}_1{}^\dagger$. One should expect $\mathbf{G}_1+\mathbf{G}_1{}^\dagger$ to have a very pronounced effect on the M orbitals.

It is very simple to put Eq. (4.7) into the more familiar eigenvalue form by arguments analogous to those used in deriving the HF equation in Sec. 3. Equation (4.6) means that

$$\mathbf{F}\psi_\mu=\sum_{\nu=1}^{M}\psi_\nu\kappa_{\nu\mu}.$$

If we construct the N-electron wave function Ψ from all of the possible Slater determinants which can be constructed from the M spin orbitals, Ψ is not affected by our choice of the ψ_μ. It is the solution to $\mathfrak{H}\Psi=E\Psi$, where $\mathfrak{H}$ is given by Eq. (2.2). The operator $\mathfrak{H}$ is invariant under replacement of the ψ_μ by a set of orbitals

$$\chi_\nu=\sum_{\mu=1}^{M}\psi_\mu C_{\mu\nu}, \quad (\nu=1, 2, \cdots, M)$$

if the matrix of $C_{\mu\nu}$'s is nonsingular,[33] since each ϱ_i is invariant under this transformation.[28] The matrix of $\kappa_{\mu\nu}$'s is Hermitian so we can diagonalize it by a unitary transformation. Thus it is always possible to find a set of orbitals such that

$$\mathbf{F}\psi_\mu=\epsilon_\mu\psi_\mu. \tag{4.8}$$

For $M\to\infty$ this equation is well defined, although Eq. (4.7) then loses its meaning. [We assume that in the limit $M\to\infty$ the ψ_μ form a complete set. In this limit $(\mathbf{1}-\varrho_1)=0$. Since $\mathbf{G}_1=0$ then, $\mathbf{F}_1$ reduces to a Hartree effective Hamiltonian.] There is of course no optimum choice of ψ_μ's if one uses a complete set of them.

If one were using a restricted MC-SCF theory, there would be a best choice for each ψ_μ. In this case Eq. (4.7) cannot be reduced to an eigenvalue problem without further manipulation. One has to take into consideration the restrictions placed on the variations of the orbitals by the restricted MC-SCF theory used. In other words one has a problem like that of open-shell HF theory.[34] However, one might still solve Eq. (4.8), then mix the M spin orbitals to get the orbitals that extremalize the energy in the restricted MC-SCF theory. In this way each iteration of the SCF calculation is broken into two steps.

To complete the discussion of this section we derive two equivalent energy expressions which involve the ϵ_μ. Note that

$$\mathrm{Tr}(\mathbf{F}_1\gamma_1)=\sum_{\mu=1}^{M}\epsilon_\mu\langle\psi_\mu|\,\gamma_1|\psi_\mu\rangle \tag{4.9}$$

$$=\mathrm{Tr}(\mathbf{h}_1\gamma_1)+\mathrm{Tr}(\mathbf{v}_{12}\gamma_1\gamma_2). \tag{4.10}$$

[33] P.-O. Löwdin, Advan. Phys. **5**, 1 (1956), see pp. 46–49.

[34] This has been recognized in connection with the antisymmetrized product of strongly orthogonal geminals approximation. S. Huzinaga, IBM Research Paper RJ-292, 1964 (unpublished).

One may regard $\langle\psi_\mu|\gamma_1|\psi_\mu\rangle$ as an occupation number. The total energy is

$$E=\mathrm{Tr}(\mathbf{h}_1\gamma_1)+\tfrac{1}{2}\,\mathrm{Tr}(\mathbf{v}_{12}\Gamma_{12}). \tag{4.11}$$

Combining Eqs. (4.2), (4.9), (4.10), and (4.11) we have

$$E=\sum_{\mu=1}^{M}\epsilon_\mu\langle\psi_\mu|\gamma_1|\psi_\mu\rangle+\tfrac{1}{2}\,\mathrm{Tr}v_{12}(g_{12}-\gamma_1\gamma_2). \tag{4.12}$$

This formula bears a striking resemblance to one of the HF energy expressions. Adding Eqs. (4.11) and (4.12), then dividing by 2, yields a third expression for E.

$$E=\tfrac{1}{2}[\sum_{\mu=1}^{M}\epsilon_\mu\langle\psi_\mu|\gamma_1|\psi_\mu\rangle+\mathrm{Tr}(\mathbf{h}_1\gamma_1)+\mathrm{Tr}(\mathbf{v}_{12}\mathbf{g}_{12})]. \tag{4.13}$$

This expression also is quite similar to a HF energy expression. In addition, it differs from an expression given by McWeeny[5] only in the appearance of $\mathrm{Tr}(\mathbf{v}_{12}\mathbf{g}_{12})$.

We have derived in this section an effective one-electron Hamiltonian $\mathbf{F}_1$ which differs in functional form from the Hartree Hamiltonian through the appearance of the operator $\mathbf{G}_1+\mathbf{G}_1^\dagger$. This latter operator introduces statistical correlation (exchange) and dynamical correlation into the effective Hamiltonian in the same way. This may be desirable.[35] The statistics of the system enters the orbital equation (4.9) through the one- and two-body density matrices, which define $\mathbf{G}_1$.

5. RELATION TO HARTREE-FOCK THEORY

We showed in Sec. 3 that when $M=N$, the HF theory results. In Sec. 4 we showed how a theory closely resembling the HF theory could be constructed for $M>N$. There is no reason to expect that the orbitals of these two theories will be very similar. However, one might expect that the orbitals of Sec. 4 could be mixed in such a way as to find N new orbitals which are very close to being HF orbitals. One would expect this because it has been found that the first N natural spin orbitals are quite similar to the N occupied HF orbitals in He,[36] Be,[37] and H_2.[38] (They cannot be identical unless γ_1 and $\mathbf{F}_1^{\mathrm{HF}}$ commute.) Because of the form of Eq. (4.7), we should be able to replace $\mathbf{F}_1$ by an operator whose first N eigenfunctions are the best possible approximation to the N HF orbitals in a certain energetic sense. It can be done quite simply by a method which we have explored previously in some detail.[16,17]

We can define the orbitals φ_μ which approximate to the HF orbitals in the following way. We want the φ_μ to be linear combinations of the ψ_μ, the eigenfunctions of $\mathbf{F}_1$. If we already know the ψ_μ, then $\mathfrak{H}$ is fixed. If we approximate the eigenfunction of $\mathfrak{H}$ in question by a single Slater determinant of N orbitals and require that it extremalize the expectation value of $\mathfrak{H}$, then a HF-type equation will determine the orbitals. In this sense, these orbitals will be the best approximations to the HF orbitals that can be constructed from the M orbitals of the MC-SCF theory. They are the φ_μ. They are the SCF solutions of

$$\varrho_1\mathbf{F}_1^{\mathrm{HF}}\varrho_1\varphi_\mu=\epsilon_\mu^{\mathrm{HF}}\varphi_\mu, \tag{5.1}$$

which is just the HF equation in the finite basis set representation of the M orbitals ψ_μ.

Using the definition for the φ_μ it follows that they satisfy another eigenvalue equation also. This equation may be solved for φ_μ when the ψ_μ's are not known.[16] We define

$$\langle x_1|\gamma_1^{\mathrm{HF}}|x_1'\rangle=\sum_{\mu=1}^{N}\varphi_\mu(x_1)\varphi_\mu(x_1')^* \tag{5.2}$$

and

$$\mathbf{V}_1=\mathbf{F}_1-\mathbf{F}_1^{\mathrm{HF}}. \tag{5.3}$$

(It should be understood that here $\mathbf{F}_1^{\mathrm{HF}}$ is a functional of the φ_μ, not the true HF orbitals.) With $\mathbf{F}_1$ defined as in Sec. 4, and $\mathbf{F}_1^{\mathrm{HF}}$ as in Sec. 3, then

$$\mathbf{V}_1=\mathrm{Tr}_2\mathbf{v}_{12}(\gamma_2-\gamma_2^{\mathrm{HF}})+\mathbf{A}_1+\mathbf{G}_1+\mathbf{G}_1^\dagger.$$

The φ_μ are SCF solutions of

$$(\mathbf{F}_1^{\mathrm{HF}}+\mathbf{V}_1-\varrho_1\mathbf{V}_1\varrho_1)\varphi_\mu=\epsilon_\mu^{\mathrm{HF}}\varphi_\mu. \tag{5.4}$$

The eigenvalues of Eqs. (5.1) and (5.4) are identical. Equation (5.4) should be solved to self-consistency for M orbitals, which will yield the same ϱ_1 as the ψ_μ. There will be N φ_μ which will approximate the N occupied HF orbitals.

The advantage of writing down Eq. (5.4) is that we may inspect the operators to see what causes the φ_μ to differ from the HF orbitals, and the ψ_μ from the φ_μ. First we remark that $\varrho_1\mathbf{V}_1\varrho_1$ partially cancels the effect of $\mathbf{V}_1$.[16,19] If $\mathbf{V}_1-\varrho_1\mathbf{V}_1\varrho_1$ vanished, the φ_μ and ψ_μ would be identical with each other, and with the HF orbitals. In $\mathbf{V}_1$ the Coulomb potential due to the charge distribution $\gamma_2-\gamma_2^{\mathrm{HF}}$ appears. We expect this potential to be quite small since the HF approximation yields relatively accurate charge densities,[39,40] and since $\gamma_2-\gamma_2^{\mathrm{HF}}$ is a charge distribution of zero net charge. The exchange operator $\mathbf{A}_1$ should be cancelled in part by $\mathbf{G}_1+\mathbf{G}_1^\dagger$. If we had chosen to define $\mathbf{F}_1$ differently and had introduced an exchange operator constructed from γ_2 as $\mathbf{A}_1$ is constructed from γ_2^{HF}, then $\mathbf{V}_1$ would have contained an exchange potential due to $\gamma_2-\gamma_2^{\mathrm{HF}}$. As in the case of the Coulomb potential, we would expect this exchange potential to have a relatively small effect in causing the ψ_μ and φ_μ to differ. Thus our failure to

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include an exchange term in $\mathbf{F}_1$ similar to that in $\mathbf{F}_1^{HF}$ will cause the ψ_μ and φ_μ to differ more than they might have. However we do not feel that this is a sufficiently good reason at this point to include such an exchange term. Furthermore, to choose that form of exchange potential would make the theory less general, in that it would be linked in a special way to closed-shell and unrestricted HF theory. The ψ_μ and φ_μ will not differ due to the correlation potential $\mathbf{G}_1+\mathbf{G}_1^\dagger$, because as $\mathbf{G}_1$ is defined, $\rho_1\mathbf{G}_1\rho_1=0$, i.e., it is not partially cancelled. It is $\mathbf{G}_1+\mathbf{G}_1^\dagger$ that will cause the φ_μ to differ from the HF orbitals. We can expect its effect to be most pronounced in the case of the $M-N$ φ_μ which are not occupied in the HF wave function. (This is certainly the case with the $2p$ orbitals used by Watson in his Be calculation.[13])

Equation (5.4) may be solved instead of Eq. (4.8) in determining the orbitals from which ρ_1 is constructed. There appears to be no stronger reason than Brillouin's theorem[39] for preferring to solve Eq. (5.4) rather than Eq. (4.8). Brillouin's theorem holds within the space of the M occupied orbitals.

6. DISCUSSION

The emphasis in this article has been on formulating for a system of N identical particles, an MC-SCF theory which resembles in form the HF theory. Success in doing this raises questions which we have ignored. An obvious question is what theorems of the HF theory are valid in ours. In this section we shall ask this question, and others, and offer preliminary answers. In some cases a definitive answer will be possible only after numerical studies have been made.

One important theorem from the HF theory is Brillouin's,[39,40] which says that the first-order correction to the HF wave function contains no determinants which are singly excited relative to the ground state. It has important implications for the calculation of expectation values,[40] and for the improvement of the HF wave function and energies.[41] In MC-SCF theory we might hope to have a Brillouin's theorem with regard to "singly excited" determinants, i.e., those containing $N-1$ of the M occupied orbitals and one orbital from the complementary space. Let us try to follow Brillouin and Möller and Plesset, and use as the unperturbed Hamiltonian

$$\mathbf{H}_0=\sum_{i=1}^{N}\mathbf{F}_i.$$

Unfortunately the MC-SCF wave function is not in general an eigenfunction of this $\mathbf{H}_0$. Any single determinant of N eigenorbitals of $\mathbf{F}_1$ is an eigenfunction of $\mathbf{H}_0$, but the MC-SCF wave function is a linear combination of such determinants. Unless these determinants are degenerate eigenfunctions of $\mathbf{H}_0$, we can not use $\mathbf{H}_0$ as the zeroth-order Hamiltonian of our MC-SCF wave function. For these cases in which $\mathbf{H}_0$ is a valid zeroth-order Hamiltonian, we have to show that the matrix elements of the perturbing potential $\mathbf{V}=\mathbf{H}-\mathbf{H}_0$ between the MC-SCF wave function and singly excited determinants vanish. This appears to be possible only for a zeroth-order wave function which is a single determinant. We conclude that Brillouin's theorem does not generalize to MC-SCF theory.

Although Brillouin's theorem is not valid in MC-SCF theory, there is an interesting theorem concerning the perturbation correction to the MC-SCF wave function and energy. We define the zeroth-order Hamiltonian to be $\mathfrak{H}$ [see Eq. (2.2)] and the perturbation to be

$$\mathbf{V}=\mathbf{O}\mathbf{H}(1-\mathbf{O})+(1-\mathbf{O})\mathbf{H}\mathbf{O}.$$

Let $E^{(n)}$ be the nth-order correction to the energy, and $\Psi^{(n)}$, to the wave function, in the Schrödinger perturbation theory applied to $\mathfrak{H}+\mathbf{V}$. Require that each $\Psi^{(n)}$ be orthogonal to the MC-SCF function $\Psi^{(0)}$. Then the following may be proven.

1. $E^{(n)}=0$ for n an odd integer.
2. $\mathbf{O}\Psi^{(n)}=0$ for n an odd integer.
3. $\mathbf{O}\Psi^{(n)}=\Psi^{(n)}$ for n an even integer.

This implies that a whole set of singly, doubly, and even N-tuply excited determinants do not contribute to $\Psi^{(1)}$. These results are of course a direct consequence of our choice of $\mathfrak{H}$ as the zeroth-order Hamiltonian. (A full discussion of this choice and its consequences is given in a separate article.[42]) This appears to be the closest thing to Brillouin's theorem that we can prove for MC-SCF functions.

Another theorem of great importance in HF theory is that due to Koopmans.[43] By relating the orbital eigenvalues ϵ_μ^{HF} to ionization potentials, Koopman's theorem allows us to confuse orbitals and particles. This yields of course a physical interpretation. In MC-SCF theory there does not seem to be the possibility of generally correlating single-particle levels with the energy levels of the system as a whole. This is a problem in the restricted MC-SCF theories, too. However, from the results of many-body theory one is led to hope that there is a choice of $\mathbf{F}_1$ which will yield orbital eigenvalues corresponding to energy levels. We are currently studying numerically such a possible choice of $\mathbf{F}_1$ for electronic systems. We will present the argument for this choice of $\mathbf{F}_1$ after the preliminary numerical studies have been completed. If our choice is correct, the theorem will not be as general as Koopman's, but it may have just as far reaching consequences for the physical understanding of the MC-SCF theory. In addition it should have important implications for band theory and for the assumption of Σ-Π separability.

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An important property of the HF wave function for fermions is that for closed-shell systems, and in the unrestricted HF theory, any set of N orbitals may be used in constructing the wave function so long as they yield the same ϱ_1. This property was first noted by Fock.[44] It has led to the introduction of equivalent orbitals[45] and other localized orbitals.[46] The MC-SCF theory is based on a Hamiltonian $\mathfrak{H}$, which depends on ϱ_i, but not on the particular set of M orbitals used in constructing ϱ_i. When all possible N-body wave functions which can be constructed from the M orbitals are used in forming the wave function, and the linear coefficients are chosen to minimize the energy, the wave function is independent of the choice of the M orbitals. Accordingly we can introduce localized orbitals into the MC-SCF theory. Of course the eigenfunctions of $\mathbf{F}_1$ should not be localized anymore than HF orbitals are. The situation is different for restricted MC-SCF theories.

For restricted MC-SCF wave functions, such as those constructed from strongly orthogonal geminals,[8] or from alternant molecular orbitals,[9] there is a best choice of the M orbitals. We have remarked on this in Sec. 4. The restricted MC-SCF theories are of great practical significance, since they are the only ones that we can hope to apply to large systems. (For example the alternant-molecular-orbital method has been applied to metallic hydrogen.[47] It was not an SCF calculation, of course.) We expect that the best orbitals to use in a restricted MC-SCF calculation will be more localized than the eigenfunctions of $\mathbf{F}_1$. Localization in this case is a means of introducing some correlation between the particles. The relationship of this localization to the various localization conditions introduced in the HF theory is just beginning to be explored.[48]

We wish to emphasize that the fundamental condition of MC-SCF theory, the condition on ϱ_i which we have derived, applies to the restricted MC-SCF theories, too. It suggests a resolution of restricted MC-SCF computations into two parts. First, one should compute the eigenfunctions of $\mathbf{F}_1$. Then one should transform the M occupied eigenfunctions of $\mathbf{F}_1$ so that they will minimize the total energy of the system in the restricted MC-SCF approximation. This procedure recalls that used in Löwdin's alternant-molecular-orbital approximation. The restricted MC-SCF theories will be examined in some detail in succeeding articles.

In addition to questions concerning the similarities between HF theory and MC-SCF theory, one may wonder about the bearing of MC-SCF theory on more accurate theories and concepts. At this time we can comment on the relationship between natural spin orbitals[4] and the eigenfunctions of $\mathbf{F}_1$. Also it seems to be appropriate to indicate that Löwdin's exact SCF theory[49] lies outside of the class of orbital theories that we have considered here.

The concept of natural spin orbitals (NSO) arises in connection with the one-body density matrix γ_1. The NSO expansion of γ_1 converges more rapidly than any other expansion of γ_1. The one-body density matrix of MC-SCF theory may be analyzed for NSO's, but there will be only M of them, and they will be approximations to the NSO's one could calculate from the exact γ_1. In contrast to NSO's, the eigenfunctions of $\mathbf{F}_1$ are natural in another sense. They optimize the convergence in the energy, not in γ_1. In order to have the approximate NSO's and the eigenfunctions of $\mathbf{F}_1$ identical, of course, one must show that $\mathbf{F}_1$ and γ_1 commute. Since there are freedoms one may take in the definition of $\mathbf{F}_1$, it may be possible to define an $\mathbf{F}_1$ which will commute with γ_1.

Löwdin's exact SCF theory is not a special case of the MC-SCF theory considered here. Although it is an orbital, single configuration theory, it is defined in a very special way. The definition is chosen to ensure that the expectation value of any one-particle operator, e.g., $\sum \mathbf{h}_i$ can be calculated exactly with the exact SCF-theory single-determinant wave function. Because the effective field used in Löwdin's theory is defined in terms of the reaction operator, we expect it to be quite different in character from the effective field we derived in Sec. 4.

In this article we believe we have succeeded in showing how to put the fundamental condition on the orbitals of MC-SCF theory into a general, useful, and reasonably transparent form. We expect that this will facilitate the investigation of other aspects of MC-SCF theory. We believe also that MC-SCF theory will be of great value in atomic and molecular investigations.

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