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Direct Minimization of the Energy Functional in LCAO-MO Density Matrix Formalism

III. All Single-Excitation Wavefunctions in Multiconfigurational Self-Consistent Field

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A general theory is presented for the optimization of the coefficients of orbitals and configuration interaction expansion in the case of multiconfiguration wavefunctions containing all single excitations. The orbital coefficients are optimized by suitable orthogonal transformations of the atomic basis; the CI coefficients are determined solving the usual secular problem. The energy minimization is performed directly by a gradient approach. The method works both for ground and excited states and no convergence difficulties are met. Computational examples are given for H_2O and H_2S molecules.

Key words: Direct minimization of energy – MC SCF formalism

1. Introduction

In two preceding papers a direct method of minimization of the energy functional has been proposed for closed and open shell systems and for a MC SCF formalism both for ground and excited states [1a, b].

In this paper the method is developed for the particular type of multiconfiguration wavefunction that contains all the singly excited configurations with respect to a principal closed-shell configuration (Sect. 2). Introducing a suitable orthogonal matrix, the optimization of the LCAO coefficients is carried out by a direct minimization of the energy expression along a gradient type approach (Sect. 3). The optimization of the CI expansion coefficients is obtained by solving the conventional eigenvalue problem. The method works both for ground and excited states (singlet or triplet) (Sects. 3 and 4).

The results of test calculations for H_2O and H_2S molecules are reported together with the main lines of the computational program (Sect. 5).

The single-excitation wavefunction has been proposed by several authors [2], and in a very recent paper by Dacre *et al.* [3] the single excitation MC SCF method is developed by direct minimization of the ground state energy, according to a procedure which is similar to that proposed by McWeeny [4] for the SCF method.

2. Theory: Energy Expression and Expectation Values for Wavefunctions with All Single Excitations

As trial wavefunction of CI type we assume the expansion

$$ {}^{1}\Psi^{(s)}(\boldsymbol{A}, \boldsymbol{C}) = a_0^{(s)}\,{}^{1}\Psi_0 + \sum_{I}^{m_0}\sum_{V}^{m_v} {}^{1}\Psi_{I,V}\, a_{VI}^{(s)}, \tag{1} $$

where the dependence upon the parameter matrices $\boldsymbol{A}$ and $\boldsymbol{C}$, which we are going to specify, is formally brought out as function argument. We consider a singlet state (the development for a triplet is similar and will be considered below) of a $2m_0$ electron system whose fundamental configuration of doubly occupied orbitals is represented by the Slater determinant

$$ {}^{1}\Psi_0 = \frac{1}{\sqrt{(2m_0)!}}\,|A\bar{A}\ldots L\bar{L}| \equiv \|A\bar{A}\ldots L\bar{L}\|. $$

We start from a given set of m orbitals (molecular orbitals (MO's), set $\{m\}$ for brevity) of which m_0 are doubly occupied, collected in the $1 \times m_0$ row vector

$$ |I\rangle = (A\ B \ldots I \ldots I' \ldots J \ldots L), $$

and $m_v = m - m_0$ are empty (virtual orbitals relative to the given doubly occupied fundamental configuration), collected in the $1 \times m_v$ row vector

$$ |V\rangle = (S\ T \ldots V \ldots V' \ldots Z). $$

The singlet configurations, formed by a given single excitation $I \to V$ of one electron from the orbital I of the set $|I\rangle$ to the orbital V of the set $|V\rangle$, have the well known form of a sum of two Slater determinants

$$ {}^{1}\Psi_{I,V} = \frac{1}{\sqrt{2}}\{\|A\bar{A}\ldots I\bar{V}\ldots L\bar{L}\| + \|A\bar{A}\ldots V\bar{I}\ldots L\bar{L}\|\}. $$

All the set $\{m\}$ orbitals are assumed to be orthonormal. In the following I, I' are used for orbitals of the set $|I\rangle$, V, V' for orbitals of the set $|V\rangle$ and M, N denote any two orbitals of the set $\{m\}$.

The expansion coefficients $a_{VI}^{(s)}$ are collected in the $m_v \times m_0$ matrix $\boldsymbol{A}^{(s)} = (a_{VI}^{(s)})$. The superscript (s) denotes the state of the system; the matrix $\boldsymbol{A}^{(s)}$ together with the coefficient $a_0^{(s)}$ is to be understood as the eigenvector (usually a column vector) associated with the energy ${}^{1}E^{(s)}$, that comes out of the CI secular equation. This point will be taken up again below: meanwhile we suppose to refer to a set $(a_0^{(s)}, \boldsymbol{A}^{(s)})$, $(a_0^{(s')}, \boldsymbol{A}^{(s')})$,… of $m_c = 1 + m_0 m_v$ (i.e. $s = 1, \ldots m_c$) eigenvectors (matrices) associated with eigenvalues ${}^{1}E^{(s)}$, ${}^{1}E^{(s')}$,…. Of course, this set is orthonormal, that is

$$ a_0^{(s)} a_0^{(s')*} + \operatorname{tr}(\boldsymbol{A}^{(s)}\boldsymbol{A}^{(s')\dagger}) = \delta_{ss'} \quad (s, s' = 1, \ldots m_c). \tag{2} $$

In the following the orbitals of the set $\{m\}$ are expanded (LCAO approximation) as linear combination of an orthonormal atomic basis set whose elements are collected in the $1 \times m$ row vector

$$ |\chi\rangle = (\chi_1 \cdots \chi_r \cdots \chi_m), \text{ with } \langle\chi|\chi\rangle = \boldsymbol{1}_m. $$

For brevity the atomic orbitals (AO's) will be denoted by r, s, t, u…. The linear combination coefficients for the I orbitals are called c_{rI} and are collected in a

$m \times m_0$ matrix $\boldsymbol{C}$; similarly the coefficients for the V orbitals are called d_{rV} and are collected in a $m \times m_v$ matrix $\boldsymbol{D}$. That is

$$|I\rangle = |\chi\rangle \boldsymbol{C} \quad \text{and} \quad |V\rangle = |\chi\rangle \boldsymbol{D}. \tag{3}$$

Introducing the definition ($\not{f}$ is the one-electron part of the Hamiltonian)

$$F_{MN} = f_{MN} + \sum_{J=1}^{m_0} (2\langle JM|JN\rangle - \langle JM|NJ\rangle)\ (M, N \in \{m\}),$$

where

$$f_{MN} = \langle M|\not{f}|N\rangle \quad \text{and} \quad F_{MN} = F_{NM},$$

the $\mathscr{H}$ matrix elements in the MO basis turn out to have the following expressions [5]

$$\langle {}^1\Psi_0|\mathscr{H}|{}^1\Psi_0\rangle = {}^1E_0 = \sum_{I=1}^{m_0} (f_{II} + F_{II}),$$

$$\langle {}^1\Psi_0|\mathscr{H}|{}^1\Psi_{I,V}\rangle = \sqrt{2}\,F_{IV} = \sqrt{2}\,F_{VI},$$

$$\langle {}^1\Psi_{I,V}|\mathscr{H}|{}^1\Psi_{I',V'}\rangle = {}^1E_0\delta_{II'}\delta_{VV'} + F_{VV'}\delta_{II'} - F_{II'}\delta_{VV'} + 2\langle I'V|V'I\rangle - \langle I'V|IV'\rangle.$$

Substituting and taking into account the normalization condition (2), the energy expression corresponding to the trial function (1) assumes the form

$$\begin{aligned} {}^1E^{(s)} = {}^1E_0 + \sqrt{2}\sum_I\sum_V (a_0^{(s)*}F_{IV}a_{VI}^{(s)} + a_0^{(s)}a_{VI}^{(s)*}F_{VI}) + \sum_I\sum_{V,V'} a_{VI}^{(s)*}F_{VV'}a_{V'I}^{(s)} - \\ \sum_{I,I'}\sum_V a_{VI}^{(s)*}F_{II'}a_{VI'}^{(s)} + \sum_{I,I'}\sum_{V,V'} a_{VI}^{(s)*}(2\langle I'V|V'I\rangle - \langle I'V|IV'\rangle)a_{V'I'}^{(s)}. \end{aligned} \tag{6}$$

If the MO expansion according to the Eqs.(5) and (6) is now introduced, the final expression of the energy turns out to be

$${}^1E^{(s)} = \mathrm{tr}[\boldsymbol{h}(\boldsymbol{R})\boldsymbol{L}^{(s)} + \boldsymbol{f}\boldsymbol{R} + \boldsymbol{G}(\boldsymbol{Q}^{(s)})\boldsymbol{Q}^{(s)\dagger}], \tag{7}$$

where the following matrices have been defined ($\boldsymbol{E}$ is a $m \times m$ matrix)

$$\begin{aligned} &\boldsymbol{R} = \boldsymbol{C}\boldsymbol{C}^\dagger,\ \boldsymbol{Q}^{(s)} = \boldsymbol{D}\boldsymbol{A}^{(s)}\boldsymbol{C}^\dagger, \\ &f_{rs} = \langle r|\not{f}|s\rangle,\ [\boldsymbol{G}(\boldsymbol{E})]_{rs} = \sum_{t,u}^{m} E_{tu}g_{ur,ts}, \text{ where } g_{ur,ts} = 2\langle ur|ts\rangle - \langle ur|st\rangle, \\ &\boldsymbol{h}(\boldsymbol{E}) = \boldsymbol{f} + \boldsymbol{G}(\boldsymbol{E}), \\ &\boldsymbol{L}^{(s)} = \boldsymbol{R} + \sqrt{2}\,a_0^{(s)*}\boldsymbol{Q}^{(s)} + \sqrt{2}\,a_0^{(s)}\boldsymbol{Q}^{(s)\dagger} + \boldsymbol{Q}^{(s)}\boldsymbol{Q}^{(s)\dagger} - \boldsymbol{Q}^{(s)\dagger}\boldsymbol{Q}^{(s)}. \end{aligned} \tag{8}$$

$\boldsymbol{Q}^{(s)}$ is a non-symmetric $m \times m$ matrix and $\boldsymbol{h}$ is the usual Hartree-Fock matrix (when $\boldsymbol{E} = \boldsymbol{R}$, of course). The matrix $\boldsymbol{R}$ contains the dependence upon the LCAO coefficients (matrix $\boldsymbol{C}$) and the matrix $\boldsymbol{Q}^{(s)}$ contains the dependence upon the CI expansion coefficients (matrix $\boldsymbol{A}^{(s)}$).

The orthonormality conditions for the orbitals

$$\boldsymbol{C}^\dagger\boldsymbol{C} = \boldsymbol{1}_{m_0},\ \boldsymbol{D}^\dagger\boldsymbol{D} = \boldsymbol{1}_{m_v},\ \boldsymbol{D}^\dagger\boldsymbol{C} = \boldsymbol{O}_{m_v},\ \boldsymbol{C}^\dagger\boldsymbol{D} = \boldsymbol{O}_{m_0}, \tag{9}$$

imply the idempotency and exclusivity of the matrices $\boldsymbol{R}$ and $\boldsymbol{R}_D = \boldsymbol{D}\boldsymbol{D}^\dagger$

$$\boldsymbol{R}^2 = \boldsymbol{R} \quad (\mathrm{tr}\boldsymbol{R} = m_0),\ \boldsymbol{R}_D^2 = \boldsymbol{R}_D \quad (\mathrm{tr}\boldsymbol{R}_D = m_v),\ \boldsymbol{R}\boldsymbol{R}_D = \boldsymbol{R}_D\boldsymbol{R} = \boldsymbol{O}. \tag{9a}$$

$\boldsymbol{R}_D$ is the projection operator in the subspace spanned by the virtual orbitals orthogonal to the space spanned by the occupied orbitals (of the projection operator $\boldsymbol{R}$), that is $\boldsymbol{R}_D = \boldsymbol{1}_m - \boldsymbol{R}$ [4]. The orthonormality conditions (2) in terms of $\boldsymbol{Q}^{(s)}$ matrices become

$$a_0^{(s)} a_0^{(s')*} + \mathrm{tr}(\boldsymbol{Q}^{(s)} \boldsymbol{Q}^{(s')\dagger}) = \delta_{ss'}. \tag{2a}$$

In multiconfiguration calculations both CI expansion coefficients $a_{VI}^{(s)}$ ($\boldsymbol{A}^{(s)}$ matrix) and LCAO coefficients c_{rI} ($\boldsymbol{R}$ matrix) have to be optimized in such a way that the energy ${}^1E^{(s)}$ becomes a minimum. Here the problem is of finding two matrices $\boldsymbol{R}$ and $\boldsymbol{Q}^{(s)}$ which minimize the energy (7) subject to the orthonormality conditions (9, 9a) and (2a). With regard to the state (s) it is convenient to put these constraints into the form

$$\begin{aligned} &\boldsymbol{R}^2 = \boldsymbol{R} \quad (\mathrm{tr}\boldsymbol{R} = m_0,\ \boldsymbol{R} = \boldsymbol{R}^\dagger) \\ &\boldsymbol{R}\boldsymbol{Q}^{(s)} = \boldsymbol{O},\ \boldsymbol{Q}^{(s)}\boldsymbol{R} = \boldsymbol{Q}^{(s)}\ (\text{or } \boldsymbol{Q}^{(s)}\boldsymbol{R}_D = \boldsymbol{O}) \\ &a_0^{(s)} a_0^{(s)*} + \mathrm{tr}(\boldsymbol{Q}^{(s)}\boldsymbol{Q}^{(s)\dagger}) = 1. \end{aligned} \tag{10}$$

It is easy to show that the conditions (10) come from Eqs.(9, 9a) and (2), and that from conditions (10) it is always possible to go back to the relations (9, 9a) and (2), with the definition of $\boldsymbol{Q}^{(s)}$ given by Eq.(8). Thus finding the two matrices $\boldsymbol{R}$ and $\boldsymbol{Q}^{(s)}$ is equivalent to optimize with respect to both $\boldsymbol{A}^{(s)}$ and $\boldsymbol{C}$.

When spatial symmetry is present the block structure of $\boldsymbol{Q}^{(s)}$ for the ground state is the same as that of $\boldsymbol{R}$; also for the excited states symmetry is readily taken into account.

When the matrices $\boldsymbol{R}$ and $\boldsymbol{Q}^{(s)}$ have been determined the expectation value of any physical quantity, represented by a one- or two-particle Hermitian operator, can be calculated in terms of them only. Let $\mathscr{M} = \sum_i \mathscr{m}_i$ a one-particle operator given as a sum of one-electron operators $\mathscr{m}_i$, its average value relative to the state (s) has the expression

$$\langle {}^1\Psi^{(s)} | \mathscr{M} | {}^1\Psi^{(s)} \rangle = \mathrm{tr}[\boldsymbol{m}(\boldsymbol{L}^{(s)} + \boldsymbol{R})],$$

where $\boldsymbol{m}$ is the matrix of elements $m_{rs} = \langle r | \mathscr{m}_i | s \rangle$.

Similarly, for a two-particle operator $\mathscr{B} = \sum_{i>j} \mathscr{b}_{ij}$ given as a sum of two-electron operators $\mathscr{b}_{ij}$, its average value is

$$\langle {}^1\Psi^{(s)} | \mathscr{B} | {}^1\Psi^{(s)} \rangle = \mathrm{tr}[\boldsymbol{G}_b(\boldsymbol{R})\boldsymbol{L}^{(s)} + \boldsymbol{G}_b(\boldsymbol{Q}^{(s)})\boldsymbol{Q}^{(s)\dagger}],$$

where $[\boldsymbol{G}_b(\boldsymbol{E})]_{rs} = \sum_{t,u} E_{tu}(2\langle ur | \mathscr{b}_{ij} | ts \rangle - \langle ur | \mathscr{b}_{ij} | st \rangle)$.

In particular, the transition moment between states (s) and (s') associated with the dipole operator $\mathscr{T} = \sum_i \mathscr{t}_i$ can be expressed as

$$\langle {}^1\Psi^{(s)} | \mathscr{T} | {}^1\Psi^{(s')} \rangle = \mathrm{tr}[\boldsymbol{t}(\sqrt{2}\, a_0^{(s)*} \boldsymbol{Q}^{(s')} + \sqrt{2}\, a_0^{(s')} \boldsymbol{Q}^{(s)\dagger} + \boldsymbol{Q}^{(s')}\boldsymbol{Q}^{(s)\dagger} - \boldsymbol{Q}^{(s)\dagger}\boldsymbol{Q}^{(s')})],$$

where $\boldsymbol{t}$ is the matrix of elements $t_{rs} = \langle r | \mathscr{t}_i | s \rangle$.

For a triplet state the development goes in a perfectly similar manner as before.

Here we gather the corresponding expressions:

$$
\begin{aligned}
&{}^3\Psi^{(s)}=\sum_{I}^{m_O}\sum_{V}^{m_v}{}^3\Psi_{\mathrm{I,V}}a^{(s)}_{\mathrm{VI}},\ \text{with}\ \mathrm{tr}(\boldsymbol{A}^{(s)}\boldsymbol{A}^{(s')\dagger})=\delta_{ss'},\\
&{}^3\Psi_{I,V}=\|A\bar{A}\ldots V\bar{I}\ldots L\bar{L}\|,\\
&\langle{}^3\Psi_{I,V}|\mathscr{H}|{}^3\Psi_{I',V'}\rangle=\langle{}^1\Psi_0|\mathscr{H}|{}^1\Psi_0\rangle\delta_{II'}\delta_{VV'}+F_{VV'}\delta_{II'}-F_{II'}\delta_{VV'}-\langle I'V|IV'\rangle,\\
&{}^3E^{(s)}=\mathrm{tr}\{\boldsymbol{h}(\boldsymbol{R})[\boldsymbol{R}+\boldsymbol{Q}^{(s)}\boldsymbol{Q}^{(s)\dagger}-\boldsymbol{Q}^{(s)\dagger}\boldsymbol{Q}^{(s)}]+\boldsymbol{f}\boldsymbol{R}-\boldsymbol{Q}^{(s)\dagger}\boldsymbol{K}(\boldsymbol{Q}^{(s)})\},
\end{aligned}
$$

where $[\boldsymbol{K}(\boldsymbol{Q}^{(s)})]_{rs}=\sum_{t,u} Q^{(s)}_{tu}\langle ur|st\rangle$, with $\mathrm{tr}(\boldsymbol{Q}^{(s)}\boldsymbol{Q}^{(s')\dagger})=\delta_{ss'}$.

3. First-Order Changes and the Stationary-Energy Condition

The problem of minimizing the energy concerns the optimization of the linear expansion coefficients $\boldsymbol{A}^{(s)}$ and the molecular orbital coefficients $\boldsymbol{C}$ (matrix $\boldsymbol{R}$).

A. If the orbital coefficients are given, the optimal expansion coefficients $\boldsymbol{A}^{(s)}$ may be determined from the eigenvalue problem for the CI matrix, whose elements have the expressions (5).

B. The minimization of the energy with respect to the molecular orbital coefficients $\boldsymbol{C}$ can be approached introducing a $m\times m$ orthogonal matrix $\boldsymbol{U}(\boldsymbol{X})$ of the form [1]

$$\boldsymbol{U}(\boldsymbol{X})=-\mathbf{1}+2\boldsymbol{P}^{-1},\ \text{with}\ \boldsymbol{P}=\mathbf{1}+\boldsymbol{X}-\tilde{\boldsymbol{X}},\tag{11}$$

where $\boldsymbol{X}$ is an arbitrary $m\times m$ matrix. Performing the transformations

$$\bar{\boldsymbol{R}}=\boldsymbol{U}\boldsymbol{R}\tilde{\boldsymbol{U}}\ \text{and}\ \bar{\boldsymbol{Q}}^{(s)}=\boldsymbol{U}\boldsymbol{Q}^{(s)}\tilde{\boldsymbol{U}}\tag{12}$$

on the two initial matrices $\boldsymbol{R}$ and $\boldsymbol{Q}^{(s)}$, which satisfy the constraints (10), the transformed matrices (12), due to the orthogonality of $\boldsymbol{U}$, continue to satisfy the constraints (10). Substituting Eq.(12) into the energy expression (7), one has

$${}^1\bar{E}^{(s)}=\mathrm{tr}[\boldsymbol{h}(\bar{\boldsymbol{R}})\bar{\boldsymbol{L}}^{(s)}+\boldsymbol{f}\bar{\boldsymbol{R}}+\boldsymbol{G}(\bar{\boldsymbol{Q}}^{(s)})\bar{\boldsymbol{Q}}^{(s)\dagger}].\tag{13}$$

The matrix transformations (12) are equivalent to an orthogonal transformation made on the full atomic basis $|\chi\rangle$; namely, if $|\chi\rangle\rightarrow|\chi\rangle\boldsymbol{U}$, the transformations induced on the molecular orbital coefficients are $\boldsymbol{C}\rightarrow\boldsymbol{U}\boldsymbol{C}=\bar{\boldsymbol{C}}$ and $\boldsymbol{D}\rightarrow\boldsymbol{U}\boldsymbol{D}=\bar{\boldsymbol{D}}$, so that the matrices $\boldsymbol{R}$ and $\boldsymbol{Q}^{(s)}$ are given by Eq.(12) and the energy by Eq.(13). Instead, the matrix $\boldsymbol{A}^{(s)}$ is not affected by a transformation of this kind: its invariance is immediately brought out observing that $\boldsymbol{A}^{(s)}\rightarrow\bar{\boldsymbol{A}}^{(s)}=\bar{\boldsymbol{D}}\bar{\boldsymbol{Q}}\bar{\boldsymbol{C}}^{\dagger}=\boldsymbol{A}^{(s)}$.

Let $\boldsymbol{U}\rightarrow\boldsymbol{U}+\delta\boldsymbol{U}$, where $\delta\boldsymbol{U}=2\boldsymbol{P}^{-1}\delta\boldsymbol{X}\boldsymbol{P}^{-1}+2\boldsymbol{P}^{-1}\delta\tilde{\boldsymbol{X}}\boldsymbol{P}^{-1}$, the first-order change $\delta\bar{E}^{(s)}$ of the energy with respect to the independent variables $\boldsymbol{X}$ can be worked out and, after some straightforward algebra [1], the gradient matrix $\boldsymbol{G}_x$ is obtained

$$\boldsymbol{G}_x=4\tilde{\boldsymbol{P}}^{-1}[\boldsymbol{D}_x-\tilde{\boldsymbol{D}}_x]\boldsymbol{P}^{-1},\tag{14}$$

where $\boldsymbol{D}_x=\bar{\boldsymbol{L}}^{(s)}\boldsymbol{h}(\bar{\boldsymbol{R}})+\bar{\boldsymbol{R}}\boldsymbol{h}(\bar{\boldsymbol{L}}^{(s)})+\bar{\boldsymbol{Q}}^{(s)\dagger}\boldsymbol{G}(\bar{\boldsymbol{Q}}^{(s)})+\bar{\boldsymbol{Q}}^{(s)}\boldsymbol{G}(\bar{\boldsymbol{Q}}^{(s)\dagger})$.

The minimum energy condition $\boldsymbol{G}_x=\boldsymbol{O}$ is then equivalent to the condition that $\boldsymbol{D}_x$ has to be a symmetric matrix, i.e.

$$\boldsymbol{D}_x=\tilde{\boldsymbol{D}}_x,\tag{15}$$

which yields just the necessary relations to determine the $m(m-1)/2$ elements of the arbitrary skew-symmetric matrix $\boldsymbol{X}-\tilde{\boldsymbol{X}}$.

Eq.(15) is the form assumed by the Brillouin theorem for the particular case of the theory here presented (see Ref. [1b]).

4. An Iterative Method of Solution

In order to satisfy the minimum condition (15) an iterative process can be set up according to the following steps [1].

1) The initial LCAO coefficient matrix to start with, can be obtained by diagonalizing the core part of the Hamiltonian: the matrices $\boldsymbol{C}$, $\boldsymbol{D}$ and $\boldsymbol{R}=\boldsymbol{C}\boldsymbol{C}^{\dagger}$ are computed in this way.

2) Then the CI secular problem is solved to obtain the initial matrix $A^{(s)}$ and $a_0^{(s)}$ associated with the energy ${}^1E^{(s)}$ for the ground or excited state (s) and the matrix $\boldsymbol{Q}^{(s)}$ is calculated.

3) The matrix $A^{(s)}$ so found is held fixed and the minimization process for the orbital coefficients is started with $\boldsymbol{X}=\boldsymbol{O}$, the gradient matrix $\boldsymbol{G}_x$ is computed and a new point $\boldsymbol{X}'$ is found along the chosen algorithm. With the new matrix $\boldsymbol{U}'=\boldsymbol{U}(\boldsymbol{X}')$ corresponding to $\boldsymbol{X}'$, the transformed matrices $\bar{\mathbf{R}}'=\boldsymbol{U}'\boldsymbol{R}\tilde{\boldsymbol{U}}'$ and $\bar{\boldsymbol{Q}}^{(s)'}=\boldsymbol{U}'\boldsymbol{Q}^{(s)}\tilde{\boldsymbol{U}}'$ are obtained and then employed for the new iteration. The test of convergence can be made both on the decrement $\Delta E^{(s)}$ of the energy and on the value of the gradient modulus $m_g=\mathrm{tr}(\boldsymbol{G}_x\tilde{\boldsymbol{G}}_x)$. In the calculations reported below the variable metric algorithm of Murtagh and Sargent has been applied as described in Ref. [1a].

4) When self-consistence is reached (with the previously fixed $A^{(s)}$), the $\bar{\boldsymbol{R}}$, $\bar{\boldsymbol{C}}$ and $\bar{\boldsymbol{D}}$ so found are employed to redetermine the new $A^{(s)}$. The $\bar{\boldsymbol{C}}$ and $\bar{\boldsymbol{D}}$ matrices are used for step 2; then step 3 follows. An alternative way to obtain MO's for the CI matrix elements is the diagonalization of the Hartree-Fock matrix $\boldsymbol{h}(\boldsymbol{R})$; this procedure is not always stable, especially near the minimum, but it has proved to be convenient in the first two or three CI calculations to speed up convergence.

The whole procedure is run over again until the differences $|A^{(s)\,\mathrm{new}}-A^{(s)\,\mathrm{old}}|$ (or, alternatively, the energy decrements) vanish to the prescribed accuracy.

5. Test Calculations. Discussion

A complete program (coded in FORTRAN language for a UNIVAC 1106 computer) has been written for the calculations according to the formulation presented above. This program is the third part of a general SCF program of which the first part computes all the necessary integrals and the second one performs the transformation of the integrals into the basis of the Schmidt orthonormal symmetry adapted orbitals. Calculations have been made on H_2O and H_2S molecules, mainly with the aim of testing the convergence of the method.

5.1. H_2O *Molecule*

The atomic orbital basis used is formed by $1s(7.65)$, $2s(1.74)$, $2s'(2.90)$, $2p(1.56)$, $2p'(3.60)$, $3s(1.00)$ on the oxygen atom, and $1s(1.20)$, $2s(0.80)$ on the hydrogen atoms. The molecular geometry is the experimental one: OH = 1.8111 a.u. and $\hat{HOH}$ = 104° 27′. By way of illustration of convergence behaviour of the energy minimization, we report in Table 1 some numerical results of the iterative process. The parameter α of the Table 1 has been defined in Ref. [1a]. We have found that the convergence rate may be improved by a more proper choice of the α value. The density matrix $\boldsymbol{R}$ at the starting point was obtained from the eigenvectors of the core matrix. This starting point of very bad energy has been deliberately chosen to test the reliability of the method. In Table 2 we report the values of the dipole moment of the ground state and the vertical transition energies together with their oscillator strengths. The given results are not surely accurate mainly because the chosen basis does contain neither *d* oxygen orbitals upon which the value of the dipole moment depends [6] nor some diffuse orbitals, which have proved necessary for a correct description of the excited states [7].

5.2. H_2S *Molecule*

The atomic orbital basis is the following: on the S atom 1*s*(15.541), 2*s*(5.3144), 2*p*(5.9885), 3*s*(2.1223), 3*p*(1.8273), 4*s*(0.20) and on the H atoms 1*s*(0.8), 2*s*(0.5).

Table 1. Iterative process for the energy minimization of H_2O molecule

	Energy (a.u.)	α	m_g
1st Secular Determinant	−68.0822		
Iteration n. 1	−73.5480	0.0125	648.551
15	−75.0293		11.714
2nd Secular Determinant	−75.9207		
Iteration n. 1	−75.9304	0.0075	0.817
15	−75.9400		0.014
3rd Secular Determinant	−75.9616		
Iteration n. 1	−75.9616	0.0075	0.382
5	−75.9618		0.001
4th Secular Determinant	−75.9619		
Iteration n. 1	−75.9619	0.0055	0.155
6	−75.9620		0.0007

Table 2. Numerical results for ground and excited states of the H_2O molecule

	Calc.	Exp.[a]
Total Energy (a.u.)	−75.9620	
Dipole Moment (D)	2.71	1.85 ± 0.02
Vertical Excitation Energies (eV) and Oscillator Strengths	7.85(0.0353) $^1B_1$	7.49(0.03)
	10.05(0.0000) $^1A_2$	9.1
	11.47(0.1243) $^1B_1$	9.996(0.084)
	12.34(0.0512) $^1B_2$	
	14.66(0.1934) $^1B_2$	
	17.16(0.2553) $^1A_1$	10.17
	18.49(0.0391) $^1B_2$	
	20.93(0.0270) $^1A_1$	

[a] Ref. [7].

Table 3. Iterative process for the energy minimization of H_2S molecule

	Energy (a.u.)	α	m_g
1st Secular Determinant	−396.9632		
Iteration n. 1	−397.0950	0.0065	30.0055
15	−397.5065		10.0757
2nd Secular Determinant	−397.7303		
Iteration n. 1	−397.7303	0.0050	0.0511
10	−397.7305		0.0228
3rd Secular Determinant	−397.7313		
Iteration n. 1	−397.7314	0.0050	0.00048

Table 4. Numerical results for ground and excited states of the H_2S molecule

	Calc.	Exp.[a]
Total Energy (a.u.)	−397.7314	
Dipole Moment (D)	1.38	0.98
Vertical Excitation Energies (eV) and Oscillator Strengths	6.42(0.013)$^1B_1$	6.32(0.04)
	7.29(0.000)$^1A_2$	7.85
	8.81(0.000)$^1A_2$	8.02
	9.28 $^1B_1$	9.18
	10.72 $^1B_1$	10.91
	10.72(0.042)$^1B_2$	
	11.45 $^1B_2$	
	12.54 $^1B_2$	
	13.11 $^1A_1$	

[a] From Ref. [8].

The geometrical parameters are SH = 2.5427 a.u. and $H\hat{S}H = 90° 8'$. The convergence test is reported in Table 3 and the results for the ground and excited states in Table 4. The same comments apply as above.

The results are encouraging enough to justify a further effort to improve the convergence rate of the orbital optimization, in particular near to the minimum: using the second energy derivatives could be a suitable way [1a].

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