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General Procedure for Solving the Open-Shell SCF Secular Equations

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A general iterative algorithm is found for solving the set of open-shell SCF secular equations. It is based on a sequence of matrix diagonalizations and similarity transformations.

Key words: Open-shell SCF secular equations - Iterative algorithm

1. Introduction

After Roothaan's classical paper [1] on the open-shell SCF theory much effort was devoted to find a general calculational scheme for solving the relevant secular equations. Two basically different problems are encountered in the open-shell SCF theory. One problem is related to the elimination of the off-diagonal Lagrange multipliers between various (closed and open) shells of the same symmetry. This problem was quite generally solved by Huzinaga [2].

The other problem is to find the algorithm for the numerical solutions of the resulting set of (formally) decoupled secular equations. Roothaan's solution to this problem was to construct a single secular equation with the extensive help of projection operators [1]. This idea was further elaborated by many authors (see Ref. [3] for a detailed bibliography). However, convergence difficulties often appear in this scheme since the eigenvalues of a new secular equation generally do not resemble the eigenvalues of original secular equations [4, 5]. Some improvement in the convergence is possible by adding more terms to the SCF matrix [3, 6].

Less attention was devoted to the problem of how to solve the set of open-shell secular equations directly, without the artificial construction of the secular equation discussed above. Suggestions made along this line [1, 2, 7] do not seem to solve the problem since the resulting orbitals of different shells turn out to be non-orthogonal. A general solution to this problem will be offered in the present paper.

2. Statement of the Problem

We shall limit the considerations of the present paper to the problem of solving the set of open-shell SCF secular equations as they appear in the LCAO-MO method.

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Let us assume that the set of non-empty SCF orbitals ϕ_α is partitioned into N separate subsets $K_p, p = 1, 2 \ldots N$, so that an arbitrary orthogonal (real unitary) transformation of orbitals in a given subset does not change the total wavefunction and the total energy accordingly. The open-shell problem is then characterized by a set of N secular equations [1, 2],

$$F^{(p)} | \phi_\alpha \rangle = \sum_{q \neq p}^{N\prime} \sum_{\beta \in K_q} | \phi_\beta \rangle \theta_{\beta\alpha} + \epsilon_\alpha | \phi_\alpha \rangle, \qquad \alpha \in K_p, \tag{1}$$

with $p = 1, 2, \ldots N$. The summation index q goes over all values $1, 2 \ldots N$ except the value p. Since orbitals may be assumed real in the framework of the HF method, $F^{(p)}$ will be represented by a real matrix. This matrix $F^{(p)}$ and the matrix of the Lagrange multipliers are symmetric,

$$F^{(p)}_{ij} = F^{(p)}_{ji}, \qquad \theta_{\alpha\beta} = \theta_{\beta\alpha}, \qquad \alpha \in K_p, \qquad \beta \in K_q, \qquad q \neq p. \tag{2}$$

Here the indices i, k go over all orbitals of the basis set.

The first problem encountered in solving the set of coupled equations (1) is the problem of eliminating the coupling terms caused by the off-diagonal Lagrange multipliers $\theta_{\beta\alpha}$. A general solution to this problem was given by Huzinaga [2]. Namely, from (1) and (2) it follows that

$$\begin{aligned} \theta_{\beta\alpha} &= \langle \phi_\beta | F^{(p)} | \phi_\alpha \rangle = \theta_{\alpha\beta} = \langle \phi_\alpha | F^{(q)} | \phi_\beta \rangle \\ &= \langle \phi_\beta | F^{(q)} | \phi_\alpha \rangle, \qquad \alpha \in K_p, \qquad \beta \in K_q, \qquad p \neq q. \end{aligned} \tag{3}$$

Relation (3) is satisfied only by the SCF solutions, while in the course of the iterative procedure it will not be necessarily fulfilled. As noticed by Huzinaga [2], the Lagrange multipliers may be expressed as a linear combination of expressions in (3),

$$\theta_{\beta\alpha} = (1 - \lambda_{qp}) \langle \phi_\beta | F^{(p)} | \phi_\alpha \rangle + \lambda_{qp} \langle \phi_\beta | F^{(q)} | \phi_\alpha \rangle, \qquad \alpha \in K_p, \qquad \beta \in K_q \tag{4}$$

where λ_{pq} are free parameters and $p \neq q$. With this formula for $\theta_{\beta\alpha}$ the secular equations in (1) may be formally decoupled [2] to take the following form

$$\left\{ F^{(p)} - \sum_{q \neq p}^{N\prime} \sum_{\beta \in K_q} | \phi_\beta \rangle \langle \phi_\beta | X^{qp} \right\} | \phi_\alpha \rangle = \epsilon_\alpha | \phi_\alpha \rangle, \qquad \alpha \in K_p \tag{5}$$

with $p = 1, 2 \ldots N$, and

$$X^{qp} \equiv (1 - \lambda_{qp}) F^{(p)} + \lambda_{qp} F^{(q)}. \tag{6}$$

If $\lambda_{qp} \neq 0$, the new set of equations in (5) is fully equivalent to the initial set (1), and it takes care of the symmetry $\theta_{\beta\alpha} = \theta_{\alpha\beta}$ of the Lagrange multipliers [8].

Davidson's prescription [7]

$$\lambda_{qp} = 0 \quad \text{if} \quad p > q, \qquad \lambda_{qp} = 1 \quad \text{if} \quad p < q \tag{7}$$

provides an example of the coupling operator in which certain λ_{pq} vanish, but the equivalence of Eqs. (1) and (5) is still maintained.

The operator on the left-hand side of Eq. (5) is not Hermitian. Although it is not necessary, it is desirable from the computational point of view to have Hermitian operators so that

the iterative procedure in solving the secular equations could be based on matrix diagonalizations. If the Hermitian conjugate of the second term in (5) is added to the operator, secular equations are not affected and the SCF operator becomes Hermitian [2]. Thus, the set of coupled equations (1) is transformed into the set of decoupled equations

$$G^{(p)}|\phi_\alpha\rangle = \epsilon_\alpha|\phi_\alpha\rangle, \qquad \alpha \in K_p, \qquad p = 1, 2 \ldots N \tag{8}$$

with Hermitian SCF operators

$$G^{(p)} = F^{(p)} - \sum_{q \neq p}^{N}{}' \sum_{\beta \in K_q} \{|\phi_\beta\rangle\langle\phi_\beta|X^{qp}) + (X^{qp}|\phi_\beta\rangle\langle\phi_\beta|\}. \tag{9}$$

A general iterative procedure for solving the set of equations (8) will be described in the next section.

3. Iterative Algorithm

In order to visualize more easily the iterative algorithm for solving Eq. (8), a new set of symmetric matrices $\boldsymbol{Q}^{(p)}$ is introduced,

$$Q^{(p)}_{\mu\nu} \equiv \langle\phi_\mu|G^{(p)}|\phi_\nu\rangle, \qquad p = 1, 2, \ldots N, \tag{10}$$

where the indices μ, ν go over the full set of n orbitals including the empty ones. As a consequence of the secular equations (8), the matrices $\boldsymbol{Q}^{(p)}$ have the following property when self-consistency is reached:

$$Q^{(p)}_{\mu\alpha} = \delta_{\mu\alpha}\epsilon_\alpha, \qquad \alpha \in K_p, \qquad \mu = 1, 2 \ldots n, \qquad p = 1, 2 \ldots N. \tag{11}$$

In fact, the set of relations (11) is fully equivalent to the set of secular equations (8). Indeed, using the completeness of SCF orbitals, we have from (10)

$$\sum_{\nu=1}^{n} |\phi_\nu\rangle Q^{(p)}_{\nu\alpha} = \sum_{\nu=1}^{n} |\phi_\nu\rangle\langle\phi_\nu|G^{(p)}|\phi_\alpha\rangle = G^{(p)}|\phi_\alpha\rangle. \tag{12}$$

On the other hand we find from (11)

$$\sum_{\nu}^{n} |\phi_\nu\rangle\delta_{\nu\alpha}\epsilon_\alpha = \epsilon_\alpha|\phi_\alpha\rangle \tag{13}$$

This proves the equivalence of (11) and (8).

The structure of the matrices $\boldsymbol{Q}^{(p)}$, expressed by Eqs. (11), is shown for $N = 3$ in Fig. 1a. In this figure the white fields refer to zero submatrices. Diagonal submatrices are also distinctly represented.

Before we proceed with the construction of the iterative algorithm which would lead to such a structure of matrices $\boldsymbol{Q}^{(p)}$ as represented in Fig. 1a, we shall prove one useful property of these matrices.

Theorem: If the parameters λ_{pq} in (6) have the property $\lambda_{pq} = \lambda_{qp}$, then the following relation

$$Q^{(p)}_{\beta\alpha} + Q^{(q)}_{\alpha\beta} = 0, \qquad \alpha \in K_p, \qquad \beta \in K_q, \qquad p \neq q \tag{14}$$

results from the definition (10).

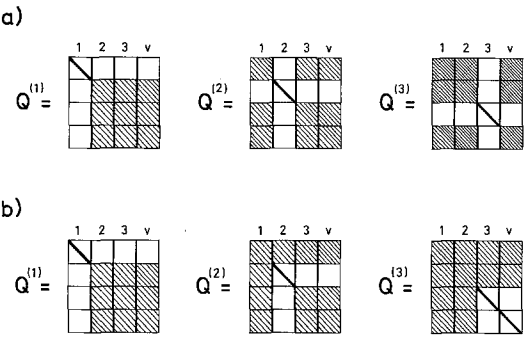

Fig. 1. Structure of matrices $Q^{(p)}$ for $N = 3$: (a) corresponding to relation (11), after the SCF solution is found: (b) before self-consistency is reached. Different sections correspond to the three shells of the non-empty orbitals (1, 2, 3) and to the shell of the virtual orbitals (v)

In order to prove this theorem it is sufficient to use definitions (10), (9) and (6), and the symmetry $F_{ij}^{(p)} = F_{ji}^{(p)}$. One finds

$$Q_{\beta\alpha}^{(p)} + Q_{\alpha\beta}^{(q)} = \langle \phi_\beta | (F^{(p)} - F^{(q)}) | \phi_\alpha \rangle (\lambda_{qp} - \lambda_{pq}), \tag{15}$$

which proves the theorem. Although the requirements of this theorem are weak indeed, it may be noticed that they are not fulfilled by Davidson's prescription, Eq. (7), and Roothaan's choice of λ_{pq} (see Ref. [8]): $\lambda_{21} = 1/(1-f)$, $\lambda_{12} = -f/(1-f)$.

The property (14) plays a fundamental role in our construction of the iterative procedure for solving Eqs. (8). Namely, although the matrices $Q^{(p)}$ exhibit the structure shown in Fig. 1a, it is sufficient to construct such an algorithm which would lead to the structure of the matrices shown in Fig. 1b. Indeed, if self-consistency is reached with an algorithm which attempts to form matrices $Q^{(p)}$ of the structures shown in Fig. 1b, the property (14) guarantees that zero-matrices will appear automatically in the corresponding places as required by Eqs. (11) and illustrated in Fig. 1a. Additional zeros of the $Q^{(3)}$ matrix in Fig. 1b result from a certain orthogonal transformation in the space of virtual orbitals, and they are irrelevant.

We shall now find the iterative procedure which forms in each iterative step the matrices $Q^{(p)}$ of the structure shown in Fig. 1b. If we introduce a basis set of n orthonormal orbitals χ_i, the secular equations (8) take the following matrix form

$$\sum_{j=1}^{n} G_{ij}^{(p)} u_{j\alpha} = \epsilon_\alpha u_{i\alpha}, \qquad \alpha \in K_p, \qquad i = 1, 2 \ldots n, \tag{16}$$

where

$$G_{ij}^{(p)} \equiv \langle \chi_i | G^{(p)} | \chi_j \rangle = F_{ij}^{(p)} - \sum_{q \neq p}^{N\,\prime} \sum_{\beta \in K_q} \sum_{k=1}^{n} \{ u_{i\beta} u_{k\beta} X_{kj}^{qp} + X_{ij}^{qp} u_{k\beta} u_{j\beta} \} \tag{17}$$

and

$$| \phi_\alpha \rangle = \sum_{i=1}^{n} u_{i\alpha} | \chi_i \rangle. \tag{18}$$

$\mathbf{u}$ is the orthogonal transformation matrix between the basis set orbitals χ_i and the SCF orbitals ϕ_α. In this basis set the matrix $Q^{(p)}$ in (10) is given by

$$Q_{\mu\nu}^{(p)} = \sum_{ij}^{n} u_{i\mu} G_{ij}^{(p)} u_{j\nu}, \qquad p = 1, 2 \ldots N; \qquad \mu, \nu = 1, 2 \ldots n. \tag{19}$$

Thus, $Q^{(p)}$ is obtained from the $G^{(p)}$ matrix by a similarity transformation. Clearly, $G^{(p)}$ itself is a function of the same matrix u which should be determined self-consistently. The purpose of the computation is to find iteratively such a matrix u which leads to the matrices $Q^{(p)}$ of the form expressed by (11). This may be achieved by the iterative procedure which consists of the following N steps:

Step 1. Construct the matrices $G^{(p)}$, Eq. (17), from the trial matrix u^0. Find the orthogonal matrix $v(1)$ which diagonalizes matrix $G^{(1)}$ through a similarity transformation like that in (19). Define matrix $u(1)$, which is identical with matrix $v(1)$.

Step k. Transform matrix $G^{(k)}$ by the similarity transformation with the matrix $u(k-1)$, generated in the previous step, into a matrix $\tilde{G}^{(k)}$. Find a new orthogonal matrix $v(k)$ of smaller dimension which diagonalizes the submatrix of $\tilde{G}^{(k)}$ in a space which excludes the orbitals of shells $K_1, K_2, \ldots K_{k-1}$. Matrix $u(k)$, which corresponds to the resulting similarity transformation of $G^{(k)}$, is given by

$$u(k) = u(k-1) \cdot \begin{pmatrix} I & 0 \\ 0 & v(k) \end{pmatrix}, \tag{20}$$

where I is the identity matrix in the space of shells $K_1, K_2, \ldots K_{k-1}$.

After all N steps are performed, the resulting matrix $u(N)$ is the new trial matrix u^0 of step 1. Iterations should be repeated until the resulting $u(N)$ matrix is equal (up to a given accuracy) to the initial matrix u^0 of that cycle.

It may be easily verified that this iterative algorithm produces in each cycle the matrices $Q^{(p)}$ of the structure shown in Fig. 1b. Namely, new similarity transformations of steps $k, k+1, \ldots$ are not able to destroy the zero submatrices in section p of matrix $Q^{(p)}$, $p<k$, which were created in step p, since these additional similarity transformations do not involve orbitals of sets $K_1, K_2 \ldots K_p \ldots K_{k-1}$. In fact, only the matrix $Q^{(N)}$ of all Q-matrices is actually constructed in this iterative procedure. However, if other matrices $Q^{(p)}$ would be formed by the similarity transformation of $G^{(p)}$ with the matrix $u(N)$, they would exhibit the structure shown in Fig. 1b. When the self-consistent matrix $u(N)$ is obtained, Eqs. (11) will be satisfied due to the property (14).

4. Conclusions

An algorithm was found for a numerical solution of the set of open-shell SCF equations. This algorithm is based on a sequence of matrix diagonalizations and similarity transformations. The procedure may be applied only if the parameters λ_{qp} in the operator X^{qp} in Eq. (6) are symmetric, $\lambda_{qp} = \lambda_{pq}$. The optimal value of these parameters should be determined by actual numerical work. It is clear, however, that they should not vanish or be close to one.

The algorithm developed here might prove to be useful also in solving orbital equations of the multi-configurational SCF scheme. Its generalization for solving the open-shell SCF equations of the complex molecular orbitals method [9, 10], which is characterized by complex non-Hermitian SCF matrices, will be reported in a separate publication.

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References

1. Roothaan, C. C. J.: Rev. Mod. Phys. **32**, 179 (1960)
2. Huzinaga, S.: J. Chem. Phys. **51**, 3971 (1969)
3. Caballol, R., Gallifa, R., Riera, J. M., Carbó, R.: Intern. J. Quantum Chem. **8**, 373 (1974)
4. Millie, P., Berthier, G.: Intern. J. Quantum Chem. **2S**, 67 (1968)
5. Sleeman, D. H.: Theoret. Chim. Acta (Berl.) **11**, 135 (1968)
6. Narita, S., Sazi, K., I'Haya, Y. J.: Chem. Phys. Letters **29**, 232 (1974)
7. Davidson, E. R.: Chem. Phys. Letters **21**, 565 (1973)
8. Albat, R., Gruen, N.: Chem. Phys. Letters **18**, 572 (1973)
9. Hendeković, J.: Intern. J. Quantum Chem. **8**, 799 (1974)
10. Hendeković, J.: Chem. Phys. Letters **32**, 597 (1975)

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