A general relation between the intrinsic convergence properties of SCF Hartree–Fock calculations and the stability conditions of their solutions

J. C. Facelli, and R. H. Contreras

Citation: The Journal of Chemical Physics **79**, 3421 (1983); doi: 10.1063/1.446190
View online: https://doi.org/10.1063/1.446190
View Table of Contents: http://aip.scitation.org/toc/jcp/79/7
Published by the American Institute of Physics

A general relation between the intrinsic convergence properties of SCF Hartree–Fock calculations and the stability conditions of their solutions

J. C. Facelli[a] and R. H. Contreras[b]

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 1, 1428 Buenos Aires, Argentina
(Received 3 January 1983; accepted 8 March 1983)

In this paper, the convergence criteria given by Stanton [J. Chem. Phys. 75, 5416 (1981)] for the Hartree–Fock SCF calculations of closed-shell systems are generalized for an unrestricted one-determinantal Hartree–Fock SCF calculation. Finally, these criteria are related to the stability conditions of the Hartree–Fock wave functions.

INTRODUCTION

There is an ever increasing amount of published papers on the stability conditions, as well as on the convergence of the SCF procedure in the Hartree–Fock equations. However, there are still some questions that deserve some consideration.

The Hartree–Fock equations can be derived from a variational principle,[1] therefore their solutions do correspond to a stationary point in the energy hypersurface. However, as only first order variations are taken into account, nothing *a priori* can be said about the nature of this stationary point which could actually be a minimum, but also could represent a maximum or a saddle point of that hypersurface.[2] Many authors have classified the different characteristics that may present the stationary point which corresponds to the solution of a Hartree–Fock problem. These studies are referenced in the literature as studies of the stability criteria of the Hartree–Fock wave functions. Pioneer among them are the works of Paldus and Cizek[3] and of Thouless.[4] Lately, the group theory has been used by Fukutone[5] to extensively study and classify them.

The second problem is related to the commonly used method to solve the Hartree–Fock equations using the SCF iterative procedure,[6] and it refers to the convergence problems that are frequently met. They have carefully been analyzed by Stanton[7,8] where a criterion for the intrinsic convergence in SCF calculations of one-determinantal closed shell wave function was considered. In one of them[8] the local criterion which guarantees the convergence of the SCF iteration cycle is stated. The relationship between this criterion and the stability conditions of the resulting Hartree–Fock solution has been discussed in a comment[9] on Stanton's paper.[8] Similar discussions for the case of a two orbital system were carried out some time ago by Bonačić-Koutecký and Koutecký[10] when studying properties of the Hartree–Fock theory in the frontier orbital model.[11]

In our comment[9] to Stanton's paper[8] it was shown that if the iterative SCF procedure converges then the Hartree–Fock solution satisfies the singlet stability condition given by Cizek and Paldus.[3] Therefore, it is concluded that all converged SCF calculation corresponds to a minimum of the energy hypersurface of the close-shell configurations, although it may be a relative minimum, different from the absolute one.

In this paper a similar discussion is carried out but seeking the relationship between a convergence criterion for the SCF iterative procedure for the most general Hartree–Fock one-determinantal wave function, which satisfies the *aufbau* principle, and its stability conditions.

THEORY

The density matrix formalism used by Löwdin[2] in deriving the stability conditions of Hartree–Fock wave functions is used. However some comments on this notation are made in order to clarify some points.

Within the one particle approximation, for an N electron system, the wave function can be written as a determinant given by

$$D = \frac{1}{\sqrt{N!}} \det\{\psi_1(X_1) \cdots \psi_N(X_N)\} , \tag{1}$$

where ψ_n are orthonormal spin orbitals, usually called the occupied spin orbitals, which satisfy

$$\langle \psi_k | \psi_n \rangle = \delta_{kn} . \tag{2}$$

Associated with these spin orbitals, a SCF calculation provides also a set of spin orbitals, $\bar{\psi}_k$ called the virtual orbitals, which span the orthogonal complement of the subspace spanned by the ψ_k and which satisfy

$$\langle \psi_n | \bar{\psi}_k \rangle = 0 ; \tag{3}$$

All these orbitals, $\{\psi_n, \bar{\psi}_k\}$ are a basis set of the whole Fock space considered in the problem. In this form, a variation of the reference determinant can be obtained[2] replacing in it each spin orbital ψ_k by ψ'_k, where

$$\psi'_k = \psi_k + C_k \bar{\psi}_k . \tag{4}$$

The density matrix for the varied determinant is given by

$$\rho' = \sum_{k=1}^{N} \psi'_k \psi'^{*}_k , \tag{5}$$

[a]Present address: Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
[b]Member of the Argentine Research Council (CONICET).

 0021-9606/83/193421-03$02.10

and it can be expanded as

$$\rho' = \rho + \delta\rho + \delta^2\rho + \cdots \ , \tag{6}$$

where $\delta\rho$ and $\delta^2\rho$ can be written in terms of the spin orbitals ψ_k and $\bar{\psi}_k$ as

$$\delta\rho = \sum_{k=1}^{N} c_k^* \psi_k \bar{\psi}_k^* + c_k \bar{\psi}_k \psi_k^* \ , \tag{7}$$

$$\delta^2\rho = \sum_{k=1}^{N} |c_k|^2 |\bar{\psi}_k \bar{\psi}_k - \psi_k \psi_k^*| \ . \tag{8}$$

The SCF equations for the spin orbitals can be written[2] in terms of the density matrix as

$$\Omega[\rho(x)]\psi_k(x_1) = \epsilon_k \psi_k(x_1) \ , \tag{9}$$

where $\Omega[\rho(x_1)]$ is the effective one electron Fock operator given by

$$\Omega[\rho(x_1)] = h_1 + \int dx_2 (1 - P_{12})\rho(x_2)/r_{12} \ , \tag{10}$$

where h_1 is the one electron part of the total Hamiltonian and P_{12} is the permutation operator that exchanges x_1 and x_2.

The usual SCF procedure consists in obtaining a solution of Eq. (9), using the density matrix calculated with the spin orbitals, which are solutions of this equation in the previous iteration. If the spin orbitals $\psi_k^{(m)}$ are the solutions of the iteration m, then those which are solution of the iteration $m+1$ satisfy

$$\Omega[\rho^{(m)}]\psi_l^{(m+1)} = \epsilon_l^{(m+1)} \psi_l^{(m+1)} \ . \tag{11}$$

It is convenient to take the first order expansion of the Eq. (11) in terms of the "true" spin orbitals, i.e., those which are the solution of the Hartree–Fock problem. Using Eq. (7) the density matrix can be written as

$$\rho^{(m)} = \rho + \sum_{k=1}^{N} [c_k^{*(m)} \psi_k \bar{\psi}_k^* + c_k^{(m)} \bar{\psi}_k \psi_k^*] = \rho + \delta\rho^{(m)} \ , \tag{12}$$

where ρ is the true density matrix and $\delta\rho^{(m)}$ may be defined as the error in the density matrix obtained in the iteration m. The effective Hamiltonian for the iteration $m+1$ becomes

$$\Omega[\rho^{(m)}] = \Omega[\rho] + \int dx_2 (1 - P_{12})\,\delta\rho^{(m)}/r_{12} \ , \tag{13}$$

$\psi_l^{(m+1)}$ can be written using Eq. (4) as

$$\psi_l^{(m+1)} = \psi_l + c_l^{(m+1)} \bar{\psi}_l \ . \tag{14}$$

Using Eqs. (12)–(14) and that the true spin orbitals satisfy the Hartree–Fock equations, Eq. (11) becomes

$$\epsilon_l \psi_l + \bar{\epsilon}_l c_l^{(m+1)} \bar{\psi}_l + \sum_{k=1}^{N} \left[c_k^{*(m)} \int dx_2 \frac{(1 - P_{12})\psi_k(2)\bar{\psi}_k^*(2)\psi_l(1)}{r_{12}} + c_k^{(m)} \int dx_2 \frac{(1 - P_{12})\bar{\psi}_k(2)\psi_k^*(2)\bar{\psi}_l(1)}{r_{12}} \right]$$
$$+ \sum_{k=1}^{N} \left[c_k^{*(m)} c_l^{(m+1)} \int dx_2 \frac{(1 - P_{12})\psi_k(2)\bar{\psi}_k^*(2)\bar{\psi}_l(1)}{r_{12}} + c_k^{(m)} c_l^{(m+1)} \int dx_2 \frac{(1 - P_{12})\bar{\psi}_k(2)\psi_k^*(2)\bar{\psi}_l(1)}{r_{12}} \right] = \epsilon_l^{(m+1)} (\psi_l + c_l^{(m+1)} \bar{\psi}_l) \ . \tag{15}$$

If operator $\int \bar{\psi}_l^*(1)\,dx_1$ is applied to Eq. (15) and the Mulliken notation[2] is introduced, then it becomes an algebraic equation relating the coefficients obtained at the iteration $m+1$ with those obtained at the iteration m:

$$c_l^{(m+1)} = \frac{(-1)}{\bar{\epsilon}_l - \epsilon_l} \sum_{k=1}^{N} [c_k^{(m)} \{(\bar{k}k|\,l\bar{l}) - (\bar{k}\bar{l}|\,lk)\}$$
$$+ c_k^{*(m)} \{(k\bar{k}|\,l\bar{l}) - (k\bar{l}|\,l\bar{k})\}] \ . \tag{16}$$

It is convenient to separate the real and imaginary parts of Eq. (16). This can be accomplished by writting the $c_k^{(m)}$ coefficients as

$$c_k^{(m)} = a_k^{(m)} + i b_k^{(m)} \tag{17}$$

and using certain QA and QB matrices

$$QA_{kl} = \frac{(-1)}{\bar{\epsilon}_l - \epsilon_l} \{(\bar{k}k|\,l\bar{l}) - (\bar{k}\bar{l}|\,lk)\} \ , \tag{18}$$

$$QB_{kl} = \frac{(-1)}{\bar{\epsilon}_l - \epsilon_l} \{(k\bar{k}|\,l\bar{l}) - (k\bar{l}|\,l\bar{k})\} \ , \tag{19}$$

which can be written as the sum of their real and imaginary parts as

$$QA = QA_1 + iQA_2 \ , \tag{20}$$

$$QB = QB_1 + iQB_2 \ . \tag{21}$$

With the notation introduced in Eqs. (17)–(21), Eq. (16) becomes

$$c_l^{(m+1)} = \sum_{k=1}^{N} [\{a_k^{(m)}[QA_1 + QB_1]_{kl} + b_k^{(m)}[-QA_2 + QB_2]_{kl}\}$$
$$+ i\{a_k^{(m)}[QA_2 + QB_2]_{kl} + b_k^{(m)}[QA_1 - QB_1]_{kl}\}] \ , \tag{22}$$

which constitutes a linear system of equations, which can be put in a matricial notation. To this end, let be defined the QT matrix

$$QT = \begin{bmatrix} QA_1 + QB_1 & -QA_2 + QB_2 \\ QA_2 + QB_2 & QA_1 - QB_1 \end{bmatrix} \ , \tag{23}$$

together with another d matrix which contains the real and imaginary parts of the c coefficients. This d matrix can be defined using the vectors a and b whose elements are the a_k and b_k coefficients

$$d = \begin{bmatrix} a & ia \\ b & -ib \end{bmatrix} \ , \tag{24}$$

then Eq. (22) adopts the compact form

$$d^{(m+1)} = QT\, d^{(m)} \ . \tag{25}$$

At this point it is important to recall some features of the $C_k^{(m)}$ coefficients, features which are carried over the d matrix. From Eqs. (12) and (14) they are associated with the error of the spin orbitals obtained at the iteration m when compared to the Hartree–Fock ones. Therefore, as it was discussed by Stanton,[8] they should

approach zero as m increases, if the SCF procedure should converge. However, in Eq. (25) it is observed that this condition is fulfilled only if all the eigenvalues of QT are, in absolute value, smaller than unity. This result comes to be the same condition required by Stanton[8] for his Q matrix in close-shell calculations.

It is interesting to inquire into the relationship between this condition and the stability conditions stated by Löwdin[2] for a general monodeterminantal spin orbital wave function. This can be undertaken paralleling the procedure used in the previous paper[9] for the close-shell problem. Let be defined two additional matrices:

$$D_{kl} = (\bar{\epsilon}_k - \epsilon_l)^{-1} \delta_{kl} \tag{26}$$

and

$$S = \begin{bmatrix} A_1 + B_1 & -A_2 + B_2 \\ A_2 + B_2 & A_1 - B_1 \end{bmatrix} , \tag{27}$$

where A_1, B_1 and A_2, B_2 are, respectively, the real and imaginary parts of the A and B matrices[2] defined by

$$A_{kl} = \{(\bar{k}k \mid l\bar{l}) - (\bar{l}\bar{k} \mid lk)\} , \tag{28}$$

$$B_{kl} = \{(k\bar{k} \mid l\bar{l}) - (k\bar{l} \mid l\bar{k})\} . \tag{29}$$

In this way the QT matrix can be written as

$$QT = D \cdot S \tag{30}$$

and the $\bar{T}$ matrix, used in Löwdin's discussion of the stability problem,[2] is given by

$$\bar{T} = D^{-1} - S , \tag{31}$$

which, after introducing the diagonal $D^{1/2}$ matrix, becomes

$$\bar{T} = D^{-1/2}(1 - D^{1/2} S D^{1/2}) D^{-1/2} . \tag{32}$$

From Eq. (32) it is straightforward to conclude,[9,12] that if the SCF calculation converges, then all eigenvalues of $(1 - D^{1/2} S D^{1/2})$ are positive, since in that case all eigenvalues of $QT = D^{1/2} S D^{1/2}$ are smaller, in absolute value, than unity. As the $\bar{T}$ matrix is obtained from $(1 - D^{1/2} S D^{1/2})$ by a pre- and a postmultiplication by $D^{-1/2}$, all its eigenvalues are also positive, provided the *aufbau* principle is satisfied, since in this case matrix D^{-1} becomes positive definite. However, this condition on the eigenvalues of $\bar{T}$ is precisely the same as that given by Löwdin[2] to guarantee the stability of the Hartree–Fock solution.

CONCLUSIONS

It is shown in the previous section that when an SCF calculation converges, then its solution is stable within the given Fock subspace, i.e., that spanned by $\{\psi_k, \bar{\psi}_k\}$. This result implies that SCF calculations always converge to local minima of the energy hypersurface. Obviously, when convergence is achieved within a certain Fock subspace nothing is implied on solutions obtained for a different Fock subspace. For instance, the convergence of a closed-shell SCF calculation, while it ensures the absence of nonreal instabilities, it does not provide any information on nonsinglet instabilities.[2,3]

It is important to recall that the close relationship found between convergence of the SCF procedure and its solution stability features, indicates how dangerous it is to enforce convergence when the SCF process presents an intrinsic[8] nonconvergent iterative result. On the other hand, if this calculation is slowly convergent, the eigenvalues of $\bar{T}$ are close to zero and it can be spoken of a "quasi" instability of the wave function within the chosen Fock subspace. In this case there are reasons to believe[13,14] that the one-determinantal representation constitutes a poor approximation for the actual wave function, because there are excited configurations which significantly contribute to the ground state of the system under consideration. In such cases a CI representation is mandatory.

Similar results presented in this paper do not provide any answer to the symmetry dilemma[13,14] because they show that convergent SCF calculations with symmetry restrictions present solutions which are local minima of the energy, but nothing is known on the existence of any other minima with different symmetry properties.

As a final point it is interesting to note that relations discussed previously for singlet[9] and nonsinglet[12] instabilities and convergence properties can be considered special cases of the more general approach presented in this paper if the spin orbitals are separated in their spatial and spin parts, as indicated in Ref. 2. The same can be said on nonreal instabilities.

ACKNOWLEDGMENTS

Grants from the Argentine Research Council (CONICET) and from the Argentine Science and Technology Secretariat (SUBCYT) are gratefully acknowledged. The comments of Professor Stanton about the manuscript of Ref. 9 are greatly appreciated.

[1] V. Fock, Z. Phys. 61, 126 (1930).
[2] P. O. Löwdin, J. L. Calais, and J. M. Calazans, Int. J. Quantum Chem. 20, 1201 (1981).
[3] J. Cizek and J. Paldus, J. Chem. Phys. 47, 3976 (1967).
[4] D. J. Thouless, *The Quantum Mechanics of Many Body Systems* (Academic, New York, 1961).
[5] H. Fukutone, Int. J. Quantum Chem. 20, 955 (1981).
[6] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
[7] R. E. Stanton, J. Chem. Phys. 75, 3426 (1981).
[8] R. E. Stanton, J. Chem. Phys. 75, 5416 (1981).
[9] J. C. Facelli and R. H. Contreras, J. Chem. Phys. 77, 1076 (1982).
[10] V. Bonačić-Koutecký and J. Koutecký, Theor. Chim. Acta 36, 163, 149 (1975).
[11] J. A. Pople, Int. J. Quantum Chem. 58, 175 (1971).
[12] G. E. Scuseria and R. H. Contreras, Theor. Chim. Acta 59, 437 (1981).
[13] P. O. Löwdin, Rev. Mod. Phys. 35, 469 (1963).
[14] P. O. Löwdin, Adv. Chem. Phys. 14, 283 (1969).