Journal of Mathematical Chemistry 13 (1993) 317–330

Functional analysis concepts and Hartree–Fock instability conditions

G. Magela e Silva [a], L.A.C. Malbouisson [b], A. Naves de Brito [a] and J.D.M. Vianna [a]

[a] *Departamento de Fisica, Instituto de Ciencias Exatas, Universidade de Brasilia, 70910 Brasilia, DF Brazil*

[b] *Instituto de Fisica, Universidade Federal da Bahia, Campus de Ondina, 40210 Salvador, BA Brazil*

Received 6 October 1992

Concepts of functional analysis, namely, regular points, tangent subspaces, constraint surfaces, Lagrangian matrix restricted to the tangent subspace of a constraint surface, are presented in connection with the Hartree–Fock (HF) problem. The energy functional in LCAO approximation is considered to be a polynomial function of several variables subject to subsidiary conditions. General HF equations and instability conditions for the unrestricted Hartree–Fock (UHF) solutions are derived from this standpoint.

1. Introduction

It is well known that Hartree–Fock (HF) solutions can present instabilities [#1]. Since the appearance of the classical work by Thouless [2] deriving the Hartree–Fock instability conditions by using variational methods, several authors [1,3–11] have performed studies of those conditions and their physical consequences. In particular, Fukutome [6,7] by utilizing the group theory has classified the possible unrestricted HF (UHF) solutions into eight classes and studied their corresponding type of instabilities.

The mathematical formulation of the HF instability conditions is achieved in terms of the second variation of the energy functional (in the Born–Oppenheimer approximation)

$$E[\Psi] = \frac{\langle \Psi | \mathbf{H}_n | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{1}$$

[#1] There is an enormous literature on the subject. Consult, for example, a recent review by Paldus [1].

where $\mathbf{H}_n$ is an n-particle Hamiltonian and $|\Psi\rangle$ is a trial function consisting of a single Slater determinant, i.e. and antisymmetrized product of n single particle functions $\{\psi_j\}$ $j = 1, \ldots, n$ such that

$$\langle\psi_i|\psi_j\rangle = \int \mathrm{d}v\, \psi_i^* \psi_j = \delta_{ij}\,. \tag{2}$$

In practice, the minimization in (1) is carried out using a finite-dimensional subspace of a general one-electron Hilbert space. One common restriction, particularly for molecular calculations, is to require that the molecular orbital (MO) ψ_j is a linear combination of atomic orbitals (LCAO) χ_μ, i.e. (in this work the MO indices, i, j, k, and l vary from 1 to n and the AO Greek indices from 1 to m)

$$\psi_k = \sum_\mu \chi_\mu C_{\mu k} \tag{3}$$

and to choose the coefficients $\{C_{\mu j}\}$ so as to minimize (1). This is the SCF–LCAO–MO approximation.

Using relation (3) for ψ_j, we note that the functional $E[\Psi]$ can be considered to be a polynomial function in the mn variables $C_{\mu j}$. Therefore, instead of studying the HF instability problem as a variational one, we can formulate it as a maximum–minimum problem of the real-valued function $E(X) = E[\Psi]$, $X = \{C_{\mu j}\}$, subject to constraints

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} = \sum_{\nu\mu} C_{\mu i}^* S_{\mu\nu} C_{\nu j}\,.$$

We call such an approach the maximum–minimum formulation (MMF).

We remark that although the MM formulation appears to be a more laborious procedure than the variational method, it has certain advantages; for instance: (i) there is a well-known and relatively simple mathematical theory to determine local [12,13] and, in some cases, global [12] extremum values of functions subject to subsidiary conditions; (ii) it gives a geometric interpretation to the unoccupied molecular orbitals; (iii) it makes possible, in principle, to develop for HF equations new methods and convergence criteria based on theorems of constrained continuous variable functions; and (iv) more important, it can indicate a route to investigate general global criteria for a point $X = \{C_{\mu k}\}$ to correspond to the absolute minimum of the energy function $E(X)$.

In this paper we derive the instability condition for UHF solutions in the framework of the MM formulation. The derivation is carried out for the case of general Hartree–Fock (GHF) method, i.e. we consider the molecular spin-orbitals (MSO) ψ as

$$\begin{aligned}\psi_k(\boldsymbol{r}, \xi) &= \varphi_k(\boldsymbol{r})\eta(\xi) + \varphi'_k(\boldsymbol{r})\eta'(\xi) \\ &\equiv |k\rangle|\eta\rangle + |k'\rangle|\eta'\rangle\,,\end{aligned} \tag{4}$$

with η and η' spin eigenfunctions; φ_k, φ'_k spatial molecular orbitals (MO) and

$$\langle\psi_k(\boldsymbol{r},\xi)|\psi_l(\boldsymbol{r},\xi)\rangle = \langle\varphi_k(\boldsymbol{r})|\varphi_l(\boldsymbol{r})\rangle + \langle\varphi'_k(\boldsymbol{r})|\varphi'_l(\boldsymbol{r})\rangle = \delta_{kl}\,. \tag{5}$$

The present paper is arranged as follows. In section 2 we formulate instability conditions at the general spin orbital (GSO) level (i.e. GHF method) by using the MM formulation. Our derivation includes three steps. First, we determine the Lagrangian matrix $\boldsymbol{L}$. Second, we construct the tangent subspace $\boldsymbol{M}$. Finally, we obtain the restriction of $\boldsymbol{L}$ to $\boldsymbol{M}$, $\boldsymbol{L}_M$, which in the MMF scheme is the instability matrix. Section 3 is devoted to comments and concluding remarks.

2. Derivation of instability conditions

Considering MSOs given by (4), let $|\boldsymbol{\Psi}\rangle$ represent a normalized Slater determinant for an n-electron system. It follows that $\langle\boldsymbol{\Psi}|\boldsymbol{\Psi}\rangle = 1$. Then, we have in the LCAO approximation, with usual notation, that

$$\begin{aligned} E[\boldsymbol{\Psi}] = {} & \sum_k \sum_{\alpha\beta} (C^*_{\alpha k} h_{\alpha\beta} C_{\beta k} + C'^*_{\alpha k} h_{\alpha\beta} C'_{\beta k}) \\ & + \tfrac{1}{2} \sum_{kl} \sum_{\alpha\beta\gamma\delta} (C^*_{\alpha k} C^*_{\gamma l} \langle\alpha\gamma\|\beta\delta\rangle_a C_{\delta l} C_{\beta k} + C'^*_{\alpha k} C'^*_{\gamma l} \langle\alpha\gamma\|\beta\delta\rangle_a C'_{\delta l} C'_{\beta k} \\ & + 2C'^*_{\alpha k} C^*_{\gamma\lambda} \langle\alpha\gamma\|\beta\delta\rangle C_{\delta l} C'_{\beta k} - 2C'^*_{\alpha k} C^*_{\gamma l} \langle\alpha\gamma\|\delta\beta\rangle C'_{\delta l} C_{\beta k}) \end{aligned} \tag{6}$$

with

$$\langle\alpha\gamma\|\beta\delta\rangle_a = \langle\alpha\gamma\|\beta\delta\rangle - \langle\alpha\gamma\|\delta\beta\rangle\,,$$

where we have considered the spin-independent Hamiltonian $\mathbf{H}_n$ given by (in atomic units)

$$\mathbf{H}_n = \sum_k h_k + \tfrac{1}{2} \sum_{kl} \frac{1}{r_{kl}}$$

and the LCAO expansions of MOs given by

$$\varphi_k = \sum_\gamma \chi_\gamma C_{\gamma k}\,,$$

$$\varphi'_k = \sum_\gamma \chi_\gamma C'_{\gamma k}, \quad \langle\chi_\mu|\chi_\mu\rangle = 1\,.$$

As the coefficients $\{C_{\mu k}, C'_{\mu k}\}$ represent the molecular orbital (MO) in the chosen basis, we shall call in this paper each set of these coefficients a molecular orbital.

The orthonormalization condition (5) in terms of $C_{\mu k}$ and $C'_{\mu k}$ is written as

$$\sum_{\alpha\beta} C^*_{\alpha k} S_{\alpha\beta} C_{\beta l} + \sum_{\alpha\beta} C'^*_{\alpha k} S_{\alpha\beta} C'_{\beta l} = \delta_{kl}\,, \tag{7}$$

where $S_{\alpha\beta}$ is the overlap matrix, $S_{\alpha\beta} = \langle\chi_\alpha|\chi_\beta\rangle$.

Let us define

$$\underline{\mathbf{C}} = (C_{11}, C_{21}, \ldots, C_{\gamma k}, \ldots, C_{mn}; C'_{11}, C'_{21}, \ldots, C'_{\gamma k}, \ldots, C'_{mn}; C^*_{11}, C^*_{21}, \ldots, C^*_{\gamma k}, \ldots, C^*_{mn}; C'^*_{11} C'^*_{21}, \ldots, C'^*_{\gamma k}, \ldots, C'^*_{mn}) = (\ldots, \underline{C}_{\lambda w}, \ldots) \tag{8}$$

with $w = 1, 2, \ldots, 4n$; $\underline{C}_{\lambda k} = C_{\lambda k}$; $\underline{C}_{\lambda, n+k} = C'_{\lambda k}$; $\underline{C}_{\lambda, 2n+k} = C^*_{\lambda k}$; and $\underline{C}_{\lambda, 3n+k} = C'^*_{\lambda k}$,

$$q_{kl}(\underline{\mathbf{C}}) = \sum_{\alpha\beta}(C^*_{\alpha k} S_{\alpha\beta} C_{\beta l} + C'^*_{\alpha k} S_{\alpha\beta} C'_{\beta l}) - \delta_{kl} = 0 \tag{9}$$

and

$$\mathbf{q}(\underline{\mathbf{C}}) = (q_{11}(\underline{\mathbf{C}}), q_{12}(\underline{\mathbf{C}}), \ldots, q_{nn}(\underline{\mathbf{C}})) . \tag{10}$$

2.1. FIRST-ORDER NECESSARY CONDITIONS

To derive the HF instability conditions in MMF scheme, we consider (6) as a function $E(\underline{\mathbf{C}})$ subject to the constraints $\boldsymbol{q}(\underline{\mathbf{C}}) = 0$ and apply the local theory of constrained minimization problems. According to theorem 1, (see appendix A) if $\underline{\mathbf{C}}$ is a local extremum point of $E(\underline{\mathbf{C}})$ subject to the constraints $\boldsymbol{q}(\underline{\mathbf{C}}) = 0$, there is a $\boldsymbol{\lambda} = (\lambda_{11}, \lambda_{12}, \ldots, \lambda_{nn})$ such that

$$\nabla E(\underline{\mathbf{C}}) + \boldsymbol{\lambda} \nabla \mathbf{q}(\underline{\mathbf{C}}) = \mathbf{0} , \tag{11}$$

where, in our notation, the product of two row vectors means scalar product (for instance, $\boldsymbol{\lambda}\nabla\mathbf{q}(\underline{\mathbf{C}}) \equiv \boldsymbol{\lambda} \cdot \nabla\mathbf{q}(\underline{\mathbf{C}})$).

In terms of components, we have from eq. (11)

$$\frac{\partial[E(\underline{\mathbf{C}}) - \sum_{kl} \epsilon_{kl} q_{kl}(\underline{\mathbf{C}})]}{\partial \underline{C}_{\lambda w}} = 0 , \tag{12}$$

where we have redefined the Lagrangian multipliers, i.e. $\lambda_{kl} = -\epsilon_{kl}$.

Substituting relations (6) and (9) into eq. (12) and carrying out the derivatives, we obtain the matrix equations

$$\mathbf{F}\mathbf{C}_k - \mathbf{G}'\mathbf{C}'_k = \mathbf{S}\mathbf{C}_k\boldsymbol{\varepsilon} \tag{13}$$

$$\mathbf{F}'\mathbf{C}'_k - \mathbf{G}\mathbf{C}_k = \mathbf{S}\mathbf{C}'_k\boldsymbol{\varepsilon} , \tag{14}$$

and corresponding complex conjugate equations. In eqs. (13) and (14) $\mathbf{F}$ ($\mathbf{F}'$) is the matrix which collects all Fock operator matrix elements defined in terms of $\mathbf{C}$ and $\mathbf{C}'$ ($\mathbf{C}'$ and $\mathbf{C}$). $\boldsymbol{\varepsilon} = \|\epsilon_{kl}\|$ is a Hermitian matrix and $\mathbf{G}$ and $\mathbf{G}'$ are defined as the matrices $\sum_k \sum_{\gamma\delta} C'^*_{\gamma k} \langle\alpha\gamma\|\delta\lambda\rangle C_{\delta k}$ and $\sum_k \sum_{\gamma\delta} C^*_{\gamma k} \langle\alpha\gamma\|\delta\lambda\rangle C'_{\delta k}$, respectively. The matrices $\mathbf{C}_l$ and $\mathbf{C}'_l$ are such that

$$\mathbf{C}^{\mathrm{t}}_l = (C_{1l}, C_{2l}, \ldots, C_{ml}) ,$$

$$C_l'^{\mathrm{t}} = (C'_{1l}, C'_{2l}, \ldots, C'_{ml}),$$

where the superscript t means transpose.

Equations (13) and (14) are equivalent to GHF equations [14,15] and determine the reference molecular orbitals $\{\mathbf{C}_l, \mathbf{C}'_l\}$, i.e. the point $\underline{\mathbf{C}}$ where $E(\underline{\mathbf{C}})$ has a extremum value.

By an unitary transformation, we may single out that set of coefficients $\{\mathbf{C}_l, \mathbf{C}'_l\}$ for which $\boldsymbol{\varepsilon}$ becomes diagonal, so that all the reference molecular orbitals satisfy

$$\mathbf{F}\mathbf{C}_k - \mathbf{G}'\mathbf{C}'_k = \boldsymbol{\varepsilon}\mathbf{S}\mathbf{C}_k, \tag{15}$$

$$\mathbf{F}'\mathbf{C}'_k - \mathbf{G}\mathbf{C}_k = \boldsymbol{\varepsilon}\mathbf{S}\mathbf{C}'_k, \quad \boldsymbol{\varepsilon} = \text{diagonal matrix}. \tag{16}$$

2.2. SECOND-ORDER CONDITIONS

Equations (15) and (16) correspond to first-order necessary conditions for $\underline{\mathbf{C}}$ to be a local extremum of the energy function $E(\underline{\mathbf{C}})$ subjected to the constraints $\mathbf{q}(\underline{\mathbf{C}})$ given by eq. (9). The type of local extremum point (maximum, minimum or saddle point) is characterized by the second-order conditions. Then, according to theorems 2 and 3 (appendix A) we must determine the tangent subspace $\mathbf{M}$ defined by

$$\mathbf{M} = \{\mathbf{X} : \nabla\mathbf{q}(\underline{\mathbf{C}})\mathbf{X} = \mathbf{0}\}, \tag{17}$$

and the Lagrangian matrix $\mathbf{L}(\underline{\mathbf{C}})$ defined by

$$\mathbf{L}(\underline{\mathbf{C}}) = \mathbf{E}(\underline{\mathbf{C}}) - \boldsymbol{\varepsilon}\mathbf{Q}(\underline{\mathbf{C}}), \tag{18}$$

where $\mathbf{E}(\underline{\mathbf{C}})$ and $\mathbf{Q}(\underline{\mathbf{C}})$ are the Hessian matrices associated with $E(\underline{\mathbf{C}})$ and $\mathbf{q}(\underline{\mathbf{C}})$, respectively. Furthermore, in order to apply the theorem 4 (appendix A), we must determine the restriction of $\mathbf{L}(\underline{\mathbf{C}})$ to the subspace $\mathbf{M}$, i.e. $\mathbf{L}_M$.

2.2.1. The Lagrangian matrix $\mathbf{L}(\underline{\mathbf{C}})$

The determination of $\mathbf{L}(\underline{\mathbf{C}})$ requires the construction of the Hessian matrices $\mathbf{E}(\underline{\mathbf{C}})$ and $\mathbf{Q}(\underline{\mathbf{C}})$. We observe that the $4mn$ variables $\underline{\mathbf{C}}$ can be divided into four types: $C^1_{\lambda k} = C_{\lambda k}$, $C^2_{\lambda k} = C'_{\lambda k}$, $C^3_{\lambda k} = C^*_{\lambda k}$, and $C^4_{\lambda k} = C'^*_{\lambda k}$. Thus, from the definition of Hessian matrix, we can obtain a Hermitian Hessian matrix $\mathbf{H}(\underline{\mathbf{C}})$ associated with a function $h(\underline{\mathbf{C}})$ if we arrange its elements as

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}^{31} & \mathbf{H}^{32} & \mathbf{H}^{33} & \mathbf{H}^{34} \\ \mathbf{H}^{41} & \mathbf{H}^{42} & \mathbf{H}^{43} & \mathbf{H}^{44} \\ \mathbf{H}^{11} & \mathbf{H}^{12} & \mathbf{H}^{13} & \mathbf{H}^{14} \\ \mathbf{H}^{21} & \mathbf{H}^{22} & \mathbf{H}^{23} & \mathbf{H}^{24} \end{pmatrix} = \|\mathbf{H}^{ab}\|, \quad a, b = 1, 2, 3, 4, \tag{19}$$

where $\mathbf{H}^{ab} = \|\partial^2 h(\underline{\mathbf{C}})/\partial C^a_{\lambda k}\partial C^b_{\mu l}\| \equiv \|\mathbf{H}^{ab}_{\lambda k,\mu l}\|$. (Note, for example, that

$$(\mathbf{H}^{32}_{\lambda k,\mu l})^* = \left(\frac{\partial^2 h(\underline{\mathbf{C}})}{\partial C^3_{\lambda k}\partial C^2_{\mu l}}\right)^* = \left(\frac{\partial^2 h(\underline{\mathbf{C}})}{\partial C^*_{\lambda k}\partial C'_{\mu l}}\right)^*$$
$$= \frac{\partial^2 h(\underline{\mathbf{C}})}{\partial C'^*_{\mu l}\partial C_{\lambda k}} = \frac{\partial^2 h(\underline{\mathbf{C}})}{\partial C^4_{\mu l}\partial C^1_{\lambda k}} = \mathbf{H}^{41}_{\mu l,\lambda k}\,.)$$

An analysis of the blocks $\mathbf{H}^{ab}$ allows us to conclude that there are six independent blocks only. We choose the following basic blocks: $\mathbf{H}^{11}, \mathbf{H}^{12}, \mathbf{H}^{22}, \mathbf{H}^{31}, \mathbf{H}^{41}$, and $\mathbf{H}^{42}$. Applying these general results to the Hessian of $E(\underline{\mathbf{C}})$ we have

$$(E^{11})_{\sigma k,\lambda l} = \sum_{\alpha\beta} C^*_{\alpha k}\langle\alpha\beta\|\sigma\lambda\rangle_a C^*_{\beta l}\,, \tag{20}$$

$$(E^{12})_{\sigma k,\lambda l} = \sum_{\alpha\beta}[C^*_{\alpha k}\langle\alpha\beta\|\sigma\lambda\rangle C'^*_{\beta l} - C^*_{\alpha l}\langle\alpha\beta\|\sigma\lambda\rangle C'^*_{\beta k}]\,, \tag{21}$$

$$(E^{22})_{\sigma k,\lambda l} = \sum_{\alpha\beta} C'^*_{\alpha k}\langle\alpha\beta\|\sigma\lambda\rangle_a C'^*_{\beta l}\,, \tag{22}$$

$$(E^{31})_{\sigma k,\lambda l} = F_{\sigma\lambda}\delta_{kl} - V_{\sigma l,\lambda k}\,, \tag{23}$$

$$(E^{41})_{\sigma k,\lambda l} = \sum_{\alpha\beta} C^*_{\alpha l}\langle\alpha\sigma\|\lambda\beta\rangle C'_{\beta k} - G_{\sigma\lambda}\delta_{kl}\,, \tag{24}$$

$$(E^{42})_{\sigma k,\lambda l} = F'_{\sigma\lambda}\delta_{kl} - V'_{\sigma l,\lambda k}\,, \tag{25}$$

where in eq. (23)

$$V_{\sigma k,\lambda l} = \sum_{\alpha\beta}(C^*_{\alpha k}\langle\alpha\sigma\|\beta\lambda\rangle_a C_{\beta l} + C'^*_{\alpha k}\langle\alpha\sigma\|\beta\lambda\rangle C'_{\beta l})\,, \tag{26}$$

$$F_{\sigma\lambda} = h_{\sigma\lambda} + \sum_p\sum_{\alpha\beta}(C^*_{\alpha p}\langle\alpha\sigma\|\beta\lambda\rangle_a C_{\beta p} + C'^*_{\alpha p}\langle\alpha\sigma\|\beta\lambda\rangle C'_{\beta p})\,.$$

$F_{\sigma\lambda}$ is the $\sigma\lambda$-element of the Fock operator matrix. In eq. (25) $V'_{\sigma l,\lambda k}$ is similar to $V_{\sigma l,\lambda k}$, replacing in (26) C, C^* by C', C'^* and vice versa. For the Hermitian Hessian matrix $\mathbf{Q}$ of the constraints $\mathbf{q}(\underline{\mathbf{C}})$ the only nonvanishing elements of the basic blocks are

$$(\mathbf{Q}^{31}_k)_{\sigma k,\lambda l} = S_{\sigma\lambda}\delta_{kl}\,, \tag{27}$$

$$(\mathbf{Q}^{42}_k)_{\sigma k,\lambda l} = S_{\sigma\lambda}\delta_{kl}\,. \tag{28}$$

Then, by using eqs. (18), (20)–(25), (27), and (28), we can write the Lagrangian matrix $\mathbf{L}(\underline{\mathbf{C}})$ as

$$\mathbf{L} = \begin{pmatrix} \mathbf{E}^{31} - \sum_k \varepsilon_k \mathbf{Q}_k^{31} & (\mathbf{E}^{41})^\dagger & (\mathbf{E}^{11})^\dagger & (\mathbf{E}^{12})^* \\ \mathbf{E}^{41} & \mathbf{E}^{42} - \sum_k \varepsilon_k \mathbf{Q}_k^{42} & (\mathbf{E}^{12})^\dagger & (\mathbf{E}^{22})^\dagger \\ \mathbf{E}^{11} & \mathbf{E}^{12} & (\mathbf{E}^{31} - \sum_k \varepsilon_k \mathbf{Q}_k^{31})^t & (\mathbf{E}^{41})^t \\ (\mathbf{E}^{12})^t & \mathbf{E}^{22} & (\mathbf{E}^{41})^* & (\mathbf{E}^{42} - \sum_k \varepsilon_k \mathbf{Q}_k^{42})^t \end{pmatrix}$$

$$\equiv \begin{pmatrix} \mathbf{L}^{31} & \mathbf{L}^{32} & \mathbf{L}^{33} & \mathbf{L}^{34} \\ \mathbf{L}^{41} & \mathbf{L}^{42} & \mathbf{L}^{43} & \mathbf{L}^{44} \\ \mathbf{L}^{11} & \mathbf{L}^{12} & \mathbf{L}^{13} & \mathbf{L}^{14} \\ \mathbf{L}^{21} & \mathbf{L}^{22} & \mathbf{L}^{23} & \mathbf{L}^{24} \end{pmatrix}, \tag{29}$$

where $*$ and $\dagger$ stand for complex conjugation, and Hermitian conjugation, respectively.

2.3.2. The tangent subspace **M**

In order to determine the tangent subspace **M**, we construct a basis set of vectors belonging to **M**. We note that eq. (17) gives

$$\sum_{\alpha\beta} [C^*_{\beta k} S_{\beta\alpha} X_{\alpha l} + C'^*_{\beta k} S_{\beta\alpha} X_{\alpha,l+n} + S_{\alpha\beta} C_{\beta l} X_{\alpha,k+2n} + S_{\alpha\beta} C'_{\beta l} X_{\alpha,k+3n}] = 0\,, \tag{30}$$

where $X_{\alpha w}$ $(w = 1, 2, \ldots, 4n)$ are the components of $\mathbf{X} \in \mathbf{M}$. Therefore eq. (17) is equivalent to n^2 equations given by (30), i.e. all the vectors satisfying (30) belong to tangent subspace **M**. Hence, we find readily that a basis set for **M** is given by the vectors

$$(\mathbf{d}^1_{uk})^t = (\mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}^t_u}_{k\text{th group}}, \mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}'^t_u}_{(k+n)\text{th group}}, \mathbf{0}^t, \ldots, \underbrace{\mathbf{0}^t}_{4n\text{th group}}),$$

$$(\mathbf{d}^2_{uk})^t = (\mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}^{*t}_u}_{(k+2n)\text{th group}}, \mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}'^{*t}_u}_{(k+3n)\text{th group}}, \mathbf{0}^t, \ldots, \underbrace{\mathbf{0}^t}_{4n\text{th group}}),$$

$$(\mathbf{a}_{kl})^t = (\mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}^t_k}_{l\text{th group}}, \mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{\mathbf{C}'^t_k}_{(l+n)\text{th group}}, \mathbf{0}^t, \ldots, \mathbf{0}^t \underbrace{-\mathbf{C}^{*t}_l}_{(k+2n)\text{th group}},$$

$$\mathbf{0}^t, \ldots, \mathbf{0}^t, \underbrace{-\mathbf{C}'^{*t}_l}_{(k+3n)\text{th group}}, \mathbf{0}^t, \ldots, \underbrace{\mathbf{0}^t}_{4n\text{th group}}).$$

where $u = n+1, \ldots, m$ and the symbols **0** stand for column vectors with m null elements. We note that the vectors $\mathbf{d}^1_{uk}$ and $\mathbf{d}^2_{uk}$ are constructed from unoccupied molecular orbitals and $\mathbf{a}_{kl}$ from occupied molecular orbitals. Furthermore, we can consider **M** as a direct sum of $\mathbf{M}_d$ spanned by $\{\mathbf{d}^1_{uk}\}$ and $\{\mathbf{d}^2_{uk}\}$ and, $\mathbf{M}_a$ spanned by $\{\mathbf{a}_{kl}\}$, i.e., $\mathbf{M} = \mathbf{M}_a \oplus \mathbf{M}_d$.

2.2.3. The restriction $\mathbf{L}_M$ *of* $\mathbf{L}(\underline{\mathbf{C}})$ *to* $\mathbf{M}$

A straightforward calculation shows that the restriction of $\mathbf{L}$ to subspace $\mathbf{M}_a$ is a zero matrix. Then in the matrix $\mathbf{T}$, such that $\mathbf{L}_M = \mathbf{T}^\dagger \mathbf{L} \mathbf{T}$ (see appendix A), only the vectors $\mathbf{d}^1_{uk}$ and $\mathbf{d}^2_{uk}$ need to be considered. Explicitly, we obtain for $\mathbf{T}$ the expression

$$\mathbf{T} = \begin{pmatrix} \mathbf{T}^1 & \mathbf{0} \\ \mathbf{T}^2 & \mathbf{0} \\ \mathbf{0} & \mathbf{T}^3 \\ \mathbf{0} & \mathbf{T}^4 \end{pmatrix}_{4nm \times 2n(m-n)}, \tag{31}$$

with

$$\mathbf{T}^a = (\mathbf{T}^a_{n+1} \quad \mathbf{T}^a_{n+2} \quad \dots \quad \mathbf{T}^a_m)_{nm \times (mn-n^2)}, \quad a = 1,2,3,4; \tag{32}$$

where each submatrix $\mathbf{T}^a_u$ is given by

$$\mathbf{T}^a_u = \begin{pmatrix} \mathbf{C}^a_u & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{C}^a_u & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{C}^a_u & \dots & \mathbf{0} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{C}^a_u \end{pmatrix}_{nm \times n}, \quad u = n+1, \dots, m.$$

Using $\mathbf{L}$ and $\mathbf{T}$ given by eqs. (29) and (31), respectively, we have

$$\mathbf{L}_M \equiv \begin{pmatrix} \mathbf{L}^1_M & \mathbf{L}^2_M \\ \mathbf{L}^3_M & \mathbf{L}^4_M \end{pmatrix}, \tag{33}$$

where

$$\mathbf{L}^1_M = (\mathbf{T}^3)^t \mathbf{L}^{31} \mathbf{T}^1 + (\mathbf{T}^4)^t \mathbf{L}^{41} \mathbf{T}^1 + (\mathbf{T}^3)^t \mathbf{L}^{32} \mathbf{T}^2 + (\mathbf{T}^4)^t \mathbf{L}^{42} \mathbf{T}^2, \tag{34}$$

$$\mathbf{L}^2_M = (\mathbf{T}^3)^t \mathbf{L}^{33} \mathbf{T}^3 + (\mathbf{T}^4)^t \mathbf{L}^{43} \mathbf{T}^3 + (\mathbf{T}^3)^t \mathbf{L}^{34} \mathbf{T}^4 + (\mathbf{T}^4)^t \mathbf{L}^{44} \mathbf{T}^4, \tag{35}$$

$$\mathbf{L}^3_M = (\mathbf{T}^1)^t \mathbf{L}^{11} \mathbf{T}^1 + (\mathbf{T}^2)^t \mathbf{L}^{21} \mathbf{T}^1 + (\mathbf{T}^1)^t \mathbf{L}^{12} \mathbf{T}^2 + (\mathbf{T}^2)^t \mathbf{L}^{22} \mathbf{T}^2, \tag{36}$$

$$\mathbf{L}^4_M = (\mathbf{T}^1)^t \mathbf{L}^{13} \mathbf{T}^3 + (\mathbf{T}^2)^t \mathbf{L}^{23} \mathbf{T}^3 + (\mathbf{T}^1)^t \mathbf{L}^{14} \mathbf{T}^4 + (\mathbf{T}^2)^t \mathbf{L}^{24} \mathbf{T}^4, \tag{37}$$

and we have used that $\mathbf{T}^{1\dagger} = \mathbf{T}^{3t}$ and $\mathbf{T}^{2\dagger} = \mathbf{T}^{4t}$. Each block $\mathbf{L}^a_M$ is a $n(m-n) \times n(m-n)$ matrix. We can identify an element of $\mathbf{L}^a_M$ giving its i-row and j-column $(i,j = 1,2,\dots,n(m-n))$ or specifying its subblock characterized by the values of functions $u(i), w(j)$ $(u, w = n+1, n+2, \dots, m)$ defined below and, in that uw-subblock, the $v(i)$-row and $x(j)$-column $(v, x = 1,2,\dots,n)$. The specification of $\mathbf{L}^a_M$ by using u, v, w, x-indices is more convenient in order to compare our results to those of the literature. Functions u, v, w, and x are defined by

$$u(i) = g\left(\frac{i-1}{n}\right) + n + 1, \quad v(i) = i - g\left(\frac{i-1}{n}\right)n, \tag{38}$$

$$w(j) = g\left(\frac{j-1}{n}\right) + n + 1, \quad x(j) = j - g\left(\frac{j-1}{n}\right)n, \tag{39}$$

where $g(z)$ is the integer part of z. In order to simplify the expressions of $\mathbf{L}_M^a$, we introduce the definitions

$$\mathbf{I}_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C^*_{\gamma u} C^*_{\delta w} \langle \alpha\beta \| \gamma\delta \rangle_a C_{\alpha v} C_{\beta x}, \tag{40}$$

$$\mathbf{J}_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C^*_{\gamma u} C'^*_{\delta w} \langle \alpha\beta \| \gamma\delta \rangle C_{\alpha v} C'_{\beta x}, \tag{41}$$

$$\mathbf{I}'_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C'^*_{\gamma u} C'^*_{\delta w} \langle \alpha\beta \| \gamma\delta \rangle_a C'_{\alpha v} C'_{\beta x}, \tag{42}$$

$$\mathbf{J}'_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C'^*_{\gamma u} C^*_{\delta w} \langle \alpha\beta \| \gamma\delta \rangle C'_{\alpha v} C_{\beta x}. \tag{43}$$

From eqs. (34) to (37), using eqs. (29) and (32), functions (38) and (39) as indices, and definitions (40)–(43), we get

$$\begin{aligned}(\mathbf{L}^1_M)_{ij} \equiv (\mathbf{L}^1_M)_{uwvx} &= (\epsilon_w - \epsilon_v)\delta_{uw}\delta_{xv} + \mathbf{J}_{uxvw} + \mathbf{J}'_{uxvw} + \mathbf{I}_{uxvw} \\ &\quad + \mathbf{I}'_{uxvw} - \mathbf{J}_{uxwv} - \mathbf{J}'_{uxwv},\end{aligned} \tag{44}$$

$$(\mathbf{L}^2_M)_{ij} \equiv (\mathbf{L}^2_M)_{uwvx} = \mathbf{I}_{uwvx} + \mathbf{I}'_{uwvx} + \mathbf{J}_{uwvx} + \mathbf{J}'_{uwxv} - \mathbf{J}_{uwvx} - \mathbf{J}'_{uwxv}, \tag{45}$$

$$\begin{aligned}(\mathbf{L}^4_M)_{ij} \equiv (\mathbf{L}^4_M)_{uwvx} &= (\epsilon_w - \epsilon_v)\delta_{uw}\delta_{xv} + \mathbf{J}^*_{uxvw} + \mathbf{J}'^*_{uxvw} + \mathbf{I}^*_{uxvw} \\ &\quad + \mathbf{I}'^*_{uxvw} - \mathbf{J}^*_{uxwv} - \mathbf{J}'^*_{uxwv},\end{aligned}$$

$$(\mathbf{L}^3_M)_{ij} \equiv (\mathbf{L}^3_M)_{uwvx} = \mathbf{I}^*_{uwvx} + \mathbf{I}'^*_{uwvx} + \mathbf{J}^*_{uwvx} + \mathbf{J}'^*_{uwxv} - \mathbf{J}^*_{uwvx} - \mathbf{J}'^*_{uwxv}. \tag{47}$$

From relations (44) to (47) we note that

$$\mathbf{L}^4_M = (\mathbf{L}^1_M)^* \quad \text{and} \quad \mathbf{L}^3_M = (L^2_M)^*.$$

Hence, we have from eq. (33)

$$\mathbf{L}_M = \begin{pmatrix} \mathbf{L}^1_M & \mathbf{L}^2_M \\ (\mathbf{L}^2_M)^* & (\mathbf{L}^1_M)^* \end{pmatrix}. \tag{48}$$

Matrix $\mathbf{L}_M$ with its elements defined by relations (44)–(47) is the instability matrix for the solutions of the GHF, in the MMF framework. We note that $\mathbf{L}_M$ is constructed from occupied and unoccupied LCAO–MO coefficients, orbital energies and AO integrals $\langle \alpha\beta \| \gamma\delta \rangle_a$ and $\langle \alpha\beta \| \gamma\delta \rangle$. According to theorems 2–4 (appen-

dix A) the eigenvalues of $\mathbf{L}_M$ characterize the kind of local extremum point $\underline{\mathbf{C}} = \{C_{\mu l}, C'_{\mu l}\}$ determined by eqs. (15) and (16).

Since for the other classes of HF solutions [6,7] the MOs used are special cases of the MSOs given by (4), one can derive instability matrices for each class of HF solution from (48) by imposing restrictions on the LCAO–MO coefficients. We will not present these particular instability matrices here [#2].

3. Discussion and concluding remarks

In the present paper we have considered an alternative formulation of instability conditions (the MM formulation) in order to clarify some geometrical aspects of the HF theory. Writing the energy expectation value $E[\Psi]$ in the LCAO–MO approximation, we have noted that $E[\Psi]$ can be analysed as a polynomial function of the LCAO coefficients, i.e. as a real-valued function $E(\underline{\mathbf{C}})$ defined on a complex (or real) space K^δ (the dimension of K is obtained from the number n of electrons, the number m of atomic orbitals in the LCAO basis set and the class of HF solution of interest). In consequence, the problem of HF instability conditions can be treated as a constrained minimization problem relative to the energy function. The constraint equalities are determined by n^2 orthonormalization conditions of the MSOs. This set of constraints defines a subset of K^δ which is best viewed as a hypersurface S of dimension $\delta - n^2$. Then, geometrically, we can regard a HF problem as that of the minimization of $E(\underline{\mathbf{C}})$ over the region S in K^δ defined by n^2 constraints.

The geometrical viewpoint presents at least two aspects for analysis. First, it allows us to introduce some concepts of functional analysis into quantum chemistry literature, namely the ideas of a regular point, the subspace $\mathbf{M}$ tangent to constraint surface S, and the restriction of the Lagrangian matrix $\mathbf{L}$ to the tangent subspace $\mathbf{M}$. In this context, we have shown that HF solutions are regular points of the constraints and we have characterized the tangent subspace $\mathbf{M}$ (associated with each HF solution) in terms of the gradients of the constraint functions. Next, we presented an orthonormal basis set for the subspace $\mathbf{M}$ in terms of the occupied and unoccupied molecular orbitals. We indicated that $\mathbf{M}$ is a direct sum of two vector subspaces $\mathbf{M}_a$ and $\mathbf{M}_d$, with $\mathbf{M}_d$ being spanned by the unoccupied molecular orbitals. Finally, we determined the restriction $\mathbf{L}_M$ of $\mathbf{L}$ to $\mathbf{M}$: the restriction of $\mathbf{L}$ to $\mathbf{M}_a$ is a zero matrix and the restriction to $\mathbf{M}_d$ gives the HF instability matrices known in the literature; $\mathbf{L}_M = \mathbf{T}^\dagger\mathbf{L}\mathbf{T}$, where $\mathbf{T}$ is a matrix whose columns consist of the basis vectors for $\mathbf{M}_d$.

The second aspect of the geometrical viewpoint is that it makes possible (with the functional analysis concepts above defined) to use algorithms, convergence the-

[#2] Requests for copies of a report with the particular instability matrices $\mathbf{L}_M$ and corresponding basis set for $\mathbf{M}$ should be addressed to author J.D.M. Vianna.

orems and methods of the general nonlinear constrained optimization theory to determine solutions of the HF equations; that is, it can show new relationships between the HF method and constrained minimization problems. For example, the eigenvalues of **L** restricted to **M** determine the natural rates of convergence for algorithms designed for constrained problems [12]. This result can be used in the determination of HF solutions.

This second aspect seems more important since the existence of convergence difficulties in UHF theory is well known in the literature [16,17] and in order to overcome these difficulties, it is necessary to develop new solution procedures for the HF equations. A step in this direction can be made by noting that the structure of the Lagrangian matrix restricted to the tangent subspace is the backbone of the theory of algorithms and methods for constrained problems [12,15]. Hence our interest to derive, in the MMF framework, the matrices $\mathbf{L}_M$ and corresponding basis set for **M**.

Another aspect to be considered is that the MMF can indicate a route to determine the global minimum of $E[\Psi]$. For instance, in the study of minimization problems having specified constraints we have the theorem [12]: "Consider the problem of minimization of $f(\underline{\mathbf{X}})$ subject to $g_i(\underline{\mathbf{X}}) \leqslant 0, i = 1, 2, \ldots, p$, where the functions f and g_i are convex and have continuous first partial derivatives. Suppose that $\underline{\mathbf{X}}^*$ is a regular point of the constraints. Then, a necessary and sufficient condition for $\underline{\mathbf{X}}^*$ to be a global minimum to this problem is that there exist $\mu_1 \geqslant 0, \mu_2 \geqslant 0, \ldots, \mu_p \geqslant 0$ such that

$$f(\underline{\mathbf{X}}^*) = \min\{f(\underline{\mathbf{X}}) + \mu_1 g_1(\underline{\mathbf{X}}) + \mu_2 g_2(\underline{\mathbf{X}}) + \ldots + \mu_p g_p(\underline{\mathbf{X}})\},$$

$$\mu_i g_i(\underline{\mathbf{X}}^*) = 0 \quad \text{for } i = 1, 2, \ldots, p."$$

One such result can be used in connection with our MM formulation of the HF problem. Hence, at least for some specific physical systems, the MMF can show that a HF solution is a global minimum of $E[\underline{\mathbf{C}}]$. Furthermore, we believe that the tangent subspace **M** is the fundamental concept to be analysed in order to determine conditions for the global minimum of $E[\underline{\mathbf{C}}]$. Studies in this direction are in progress and will be presented in a forthcoming paper.

Appendix A: Definitions and theorems

The following concepts and theorems [12,13] were used throughout the paper.

DEFINITION

A point $\underline{\mathbf{X}} \in \mathbf{E}^n$ (normed vector space of dimension n) satisfying the constraint $\mathbf{h}(\underline{\mathbf{X}}) = (h_1(\underline{\mathbf{X}}), h_2(\underline{\mathbf{X}}), \ldots, h_m(\underline{\mathbf{X}})) = \mathbf{0}$ is said to be a regular point of the con-

straint if the gradient vectors $\nabla h_1(\underline{\mathbf{X}}), \nabla h_2(\underline{\mathbf{X}}), \ldots, \nabla h_m(\underline{\mathbf{X}})$ are linearly independent. The gradient of f is given by

$$\nabla f(\mathbf{X}) = \left[\frac{\partial f(\mathbf{X})}{\partial X_1}, \frac{\partial f(\mathbf{X})}{\partial X_2}, \ldots, \frac{\partial f(\mathbf{X})}{\partial X_n}\right],$$

and for a vector valued function the gradient operation is carried out componentwise.

THEOREM 1

Let $\underline{\mathbf{X}}$ be a local extremum point of f subject to the constraints $\mathbf{h}(\underline{\mathbf{X}}) = 0$. Assume further that $\underline{\mathbf{X}}$ is a regular point of these constraints. Then there is a $\boldsymbol{\lambda} \in \mathbf{E}^m$ (normed vector space of dimension m) such that

$$\nabla f(\underline{\mathbf{X}}) + \boldsymbol{\lambda} \nabla \mathbf{h}(\underline{\mathbf{X}}) = 0 .$$

THEOREM 2

Suppose that $\underline{\mathbf{X}}$ is a local minimum of f subject to $\mathbf{h}(\underline{\mathbf{X}}) = \mathbf{0}$ and that $\underline{\mathbf{X}}$ is a regular point of these constraints. Then there is a $\boldsymbol{\lambda} \in \mathbf{E}^m$ such that $\nabla f(\underline{\mathbf{X}}) + \boldsymbol{\lambda} \nabla \mathbf{h}(\underline{\mathbf{X}}) = \mathbf{0}$. If we denote by $\mathbf{M}$ the tangent subspace $\mathbf{M} = \{\mathbf{Y} : \nabla \mathbf{h}(\underline{\mathbf{X}})\mathbf{Y} = \mathbf{0}\}$, then the matrix

$$\mathbf{L}(\underline{\mathbf{X}}) = \mathbf{F}(\underline{\mathbf{X}}) + \boldsymbol{\lambda} \mathbf{H}(\underline{\mathbf{X}})$$

is positive semidefinite on $\mathbf{M}$, that is, $\mathbf{Y}^{\dagger} \mathbf{L}(\underline{\mathbf{X}}) \mathbf{Y} \geqslant \mathbf{0}$ for all $\mathbf{Y} \in \mathbf{M}$. In the Lagrangian matrix $\mathbf{L}$, $\mathbf{F}$ and $\mathbf{H}$ are the Hermitian Hessians of f and $\mathbf{h}$, respectively. The Hessian of a vector valued function $\mathbf{g} = (g_1, g_2, \ldots, g_\alpha, \ldots, g_m)$ at $\mathbf{X}$ is given by

$$\mathbf{G}(\mathbf{X}) = (\mathbf{G}_1(\mathbf{X}), \mathbf{G}_2(\mathbf{X}), \ldots, \mathbf{G}_\alpha(\mathbf{X}), \ldots, \mathbf{G}_m(\mathbf{X})),$$

where each

$$\mathbf{G}_\alpha(\mathbf{X}) = \left\| \frac{\partial^2 g_\alpha}{\partial X_i \partial X_j} \right\| \quad i,j = 1,2,\ldots,n,$$

is an $(n \times n)$ matrix.

THEOREM 3

Suppose that there is a point $\underline{\mathbf{X}}$ satisfying $\mathbf{h}(\underline{\mathbf{X}}) = 0$, and a $\boldsymbol{\lambda} \in \mathbf{E}^m$ such that

$$\nabla f(\underline{\mathbf{X}}) + \boldsymbol{\lambda} \nabla \mathbf{h}(\underline{\mathbf{X}}) = 0 .$$

Suppose also that the matrix $\mathbf{L}(\underline{\mathbf{X}}) = \mathbf{F}(\underline{\mathbf{X}}) + \boldsymbol{\lambda} \mathbf{H}(\underline{\mathbf{X}})$ is positive definite on $\mathbf{M} = \{\mathbf{Y} : \nabla \mathbf{h}(\underline{\mathbf{X}})\mathbf{Y} = \mathbf{0}\}$, that is, for $\mathbf{Y} \in \mathbf{M}, \mathbf{Y} \neq \mathbf{0}$ there holds $\mathbf{Y}^{\dagger} \mathbf{L}(\underline{\mathbf{X}}) \mathbf{Y} > \mathbf{0}$. Then $\underline{\mathbf{X}}$ is a strict local minimum of f subject to $\mathbf{h}(\underline{\mathbf{X}}) = 0$.

THEOREM 4

The matrix $\mathbf{L}(\underline{\mathbf{X}})$ is positive definite (semidefinite) on $\mathbf{M}$, that is, $\mathbf{Y}^\dagger\mathbf{L}(\underline{\mathbf{X}})\mathbf{Y} > \mathbf{0}$ ($\geqslant \mathbf{0}$) for all $\mathbf{Y} \in \mathbf{M}$ if, and only if, the eigenvalues of its restriction to $\mathbf{M}$

$$\mathbf{L}_M = \mathbf{T}^\dagger\mathbf{L}\mathbf{T}$$

are >0 ($\geqslant 0$). $\mathbf{T}$ is a matrix whose columns consist of the basis vectors of the subspace $\mathbf{M}$.

Appendix B. Regular points of the constraints and HF solutions

We show that the solution of HF–Roothaan equations are regular points of the constraint (9). For the sake of simplicity we take the case in which the LCAO-coefficients are real and solutions of closed-shell systems. In this case, we have from eq. (9)

$$q_{kl} = \sum_\alpha \sum_\beta C_{\alpha k} S_{\alpha\beta} C_{\beta l} - \delta_{kl} = 0 . \tag{49}$$

Suppose by reductio ad absurdum that the gradient vectors ∇q_{kl} are linearly dependent. Then there exist $n(n+1)/2$ constants $\alpha_{k1}, \alpha_{k2}, \ldots, \alpha_{kl}$, ($k \leqslant l$, $l = 1, 2, \ldots, n$) not all vanishing, such that the linear combination $\sum_{kl} \alpha_{kl} \nabla q_{kl}$ is equal to the null vector, i.e.

$$\sum_{kl} \alpha_{kl} \nabla q_{kl} = 0, \quad k \leqslant l, l = 1, 2, \ldots, n .$$

For each pair (λ, j) we have from (49) that

$$\sum_{kl} \alpha_{kl} \frac{\partial q_{kl}}{\partial C_{\lambda j}}, \qquad k \leqslant l$$

$$= \sum_l \alpha_{jl} \sum_\beta S_{\lambda\beta} C_{\beta l} + \sum_k \alpha_{kj} \sum_\beta S_{\lambda\beta} C_{\beta k} = 0; \quad l \geqslant j \quad \text{and} \quad k \leqslant j .$$

Multiplying this equation by $C_{\lambda i}$ and summing over λ, we obtain

$$\sum_l \alpha_{jl} \delta_{il} + \sum_k \alpha_{kj} \delta_{ik} = 0, \quad l \geqslant j \quad \text{and} \quad k \leqslant j . \tag{50}$$

From eq. (50) it follows that

(a) if $i = j$, $2\alpha_{jj} = 0$,

(b) if $i > j$, $\alpha_{ji} = 0$,

(c) if $i < j$, $\alpha_{ij} = 0$.

These results are valid for any pair, $i, j = 1, 2, \ldots, n$. Then we came to a contra-

diction with the initial hypothesis which says that not all α_{kl} were null. In consequence, we have that the gradient vectors ∇q_{kl} are linearly independent and the molecular orbitals $\underline{\underline{C}} = (C_{11}, \ldots, C_{mn})$ are regular points of the constraints. Similarly, we can show that GSOs are regular points of the constraints (9).

References

[1] J. Paldus, in: *Self-Consistent Field, Theory and Applications*, eds. R. Carbo and M. Klobukowski (Elsevier, Amsterdam, 1990) pp. 1–45.
[2] D.J. Thouless, *The Quantum Mechanics of Many Body Systems* (Academic Press, New York, 1961).
[3] J. Čížek and J. Paldus, J. Chem. Phys. 47 (1967) 3976.
[4] J. Paldus and J. Čížek, J. Chem. Phys. 52 (1970) 2919.
[5] H. Fukutome, Prog. Theor. Phys. 50 (1973) 1433.
[6] H. Fukutome, Prog. Theor. Phys. 52 (1974) 115.
[7] H. Fukutome, Prog. Theor. Phys. 52 (1974) 1766.
[8] H. Fukutome, Prog. Theor. Phys. 53 (1975) 1320.
[9] H. Fukutome, M. Takahashi and T. Takabe, Prog. Theor. Phys. 53 (1975) 1580.
[10] M. Ozaki and H. Fukutome, Prog. Theor. Phys. 60 (1978) 1322.
[11] H. Fukutome, Int. J. Quant. Chem 20 (1981) 955.
[12] D.G. Luenberger, *Introduction to Linear and Nonlinear Programming* (Addison–Wesley, Reading, MA, 1973) pp. 219–236, 237, 312–316.
[13] M.R. Hestenes, *Optimization Theory: The Finite Dimensional Case* (Wiley, New York, 1975).
[14] B. Sykja and J.-L. Calais, J. Phys. C15 (1982) 3079.
[15] J.-L. Calais and B. Sykja, J. Phys. C15 (1982) 3093.
[16] J.C. Facelli and R.H. Contreras, J. Chem. Phys. 79 (1983) 3421.
[17] R.E. Stanton, J. Chem. Phys. 75 (1981) 3426.