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Functional analysis concepts and Hartree–Fock instability conditions. II: An analysis of the eight classes of solutions

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The continuation of the previous work is presented. Here the instability matrices for the eight classes of HF solutions, considering time reversal and spin symmetries, are derived and explicitly shown. These matrices are expressed in terms of LCAO coefficients. Hence they are of immediate application to the verification of instabilities in HF calculations.

1. Introduction

This work is a continuation of and a complement to the earlier one [1], hereafter referred to as paper I. In paper I we have shown that concepts of functional analysis as regular points, tangent subspaces, Lagrangian matrix restricted to the tangent subspace of a constrained surface can be used in connection with the Hartree–Fock (HF) problem. In our development the energy functional in the linear combination of atomic orbital (LCAO) approximation was considered to be a polynomial real-valued function of several variables subject to subsidiary conditions – the maximum-minimum formulation (MMF). From this standpoint we have determined the HF instability conditions at the general spin orbital (GSO) level, i.e., the general Hartree–Fock (GHF) method. These conditions are directly related to the dynamical matrix used in linearized TDHF or RPA theory [2].

In order to apply our development to analyze HF instabilities of a given calculation in a straightforward manner it is necessary to know if the different matrices for each class of HF solution can be determined from our fundamental instability matrix $\mathbf{L}_M$. This might seem quite a task since the MMF is general and does not use symmetry considerations. Here we shall demonstrate that using an unitary similarity transformation applied to $\mathbf{L}_M$ and imposing conditions on the LCAO coefficients according to a particular class of HF solution all the known instability matrices [3,4] can be obtained from $\mathbf{L}_M$, and we shall explicitly give all these

matrices in terms of LCAO coefficients. Our results are therefore of direct application to numerical HF calculations.

This work is arranged as follows. In section 2 we present a résumé of our development, that is, the maximum-minimum formulation (MMF) of the instability conditions. In section 3 we obtain and present explicitly the various instability matrices in terms of LCAO coefficients. Finally, section 4 is devoted to concluding remarks.

2. Equations of the MM formulation

In this section we present a résumé (for more details and references, see paper I) of our mathematical development, the MMF, for determining the fundamental instability condition using the general spin orbitals (GSO), i.e., in the context of the general Hartree–Fock method. Our notation is the usual one.

Let us consider the energy functional (in the Born–Oppenheimer approximation)

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

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

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

In paper I the molecular spin orbitals (MSOs) were given by

$$\begin{aligned} \psi_k(\mathbf{r}, \xi) &= \varphi_k(\mathbf{r})\eta(\xi) + \varphi'_k(\mathbf{r})\eta'(\xi) \\ &\equiv |k\rangle|\eta\rangle + |k'\rangle|\eta'\rangle , \end{aligned} \tag{3}$$

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

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

Here, we have required that the molecular orbitals φ_k, φ'_k are linear combinations of atomic orbitals (AOs) χ_μ, i.e.

$$\begin{aligned} \varphi_k &= \sum_\gamma \chi_\gamma C_{\gamma k}, \\ \varphi'_k &= \sum_\gamma \chi_\gamma C'_{\gamma k}, \quad \langle \chi_\mu | \chi_\mu \rangle = 1 . \end{aligned} \tag{4}$$

The coefficients $\{C_{\mu k}, C'_{\mu k}\}$ represent the molecular orbital (MO) in the chosen basis. These coefficients can be chosen so as to minimize (1) and we have the LCAO-MO approximation at the general spin orbital (GSO) level. (In this work, as

in paper I, the MO indices i, j, k, and l vary from one to n and the AO indices (Greek letters) from one to m (number of atomic orbitals in the LCAO basis set).)

Using relation (3) for ψ_j, we treated the functional $E[\Psi]$ as a polynomial function in the $2mn$ variables $C_{\mu j}$ and $C'_{\mu j}$. Therefore, instead of studying the HF instability problem as a variational one, we formulated it as a maximum-minimum problem of the real-valued function $E(X) = E[\Psi]$, $X = \{C_{\mu j}, C'_{\mu j}\}$, subject to constraints

$$\sum_{\alpha\beta} C^*_{\alpha k} S_{\alpha\beta} C_{\beta l} + \sum_{\alpha\beta} C'^*_{\alpha k} S_{\alpha\beta} C'_{\beta l} = \delta_{kl}, \tag{5}$$

where $S_{\alpha\beta}$ is the overlap matrix, $S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle$. We called this approach the maximum-minimum formulation (MMF) [1].

To derive the HF instability conditions in the MMF scheme, we considered $E[\Psi]$ as a function $E(X)$ subject to the constraints (5) and applied the local theory of constrained minimization problems. Thus, from the first-order conditions we obtained the GHF equations [5,6] that determine the reference molecular orbitals $\{\mathbf{C}_l, \mathbf{C}'_l\}$, i.e.,

$$\mathbf{F}\mathbf{C}_k - \mathbf{G}'\mathbf{C}'_k = \epsilon \mathbf{S}\mathbf{C}_k\,, \tag{6}$$

$$\mathbf{F}'\mathbf{C}'_k - \mathbf{G}\mathbf{C}_k = \epsilon \mathbf{S}\mathbf{C}'_k, \quad \epsilon = \text{diagonal matrix}, \tag{7}$$

where $\mathbf{F}$ ($\mathbf{F}'$) is the matrix which collects all Fock operator matrix elements defined in terms of $\mathbf{C}$ and $\mathbf{C}'$ ($\mathbf{C}'$ and $\mathbf{C}$). $\varepsilon = ||\epsilon_{kl}||$ 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 type of local extremum point (maximum, minimum or saddle point) is characterized by second-order conditions. Then, according to the MMF method, firstly we determine the Lagrangian matrix $\mathbf{L}$. Secondly, we construct the tangent subspace $\mathbf{M}$. Finally, we obtain the restriction of $\mathbf{L}$ to $\mathbf{M}$, $\mathbf{L}_M$, which in the MMF scheme is the fundamental instability matrix,

$$\mathbf{L}_M = \begin{pmatrix} \mathbf{L}^1_M & \mathbf{L}^2_M \\ (\mathbf{L}^2_M)^* & (\mathbf{L}^1_M)^* \end{pmatrix}. \tag{8}$$

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 ($i,j = 1, 2, \cdots, n(m-n)$) or specifying its sub-block characterized by the values of functions $u(i)$, $w(j)$ ($u, w = n+1, n+2, \cdots, m$) defined below and, in that uw-sub block, the $v(i)$-row and $x(j)$-column ($v, x = 1, 2, \cdots, n$). 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

$$u(i) = g\left(\frac{i-1}{n}\right) + n + 1, \quad v(i) = i - g\left(\frac{i-1}{n}\right) n\,, \tag{9}$$

$$w(j) = g\left(\frac{j-1}{n}\right) + n + 1, \quad x(j) = j - g\left(\frac{j-1}{n}\right)n, \tag{10}$$

where $g(z)$ is the integer part of z. Therefore (see paper I)

$$(\mathbf{L}_M^1)_{ij} \equiv (\mathbf{L}_M^1)_{uwvx} = (\epsilon_w - \epsilon_v)\delta_{uw}\delta_{xv} + \mathbf{J}_{uxvw} + \mathbf{J}'_{uxvw} + \mathbf{I}_{uxvw} + \mathbf{I}'_{uxvw} - \mathbf{J}_{uxwv} - \mathbf{J}'_{uxwv}, \tag{11}$$

$$(\mathbf{L}_M^2)_{ij} \equiv (\mathbf{L}_M^2)_{uwvx} = \mathbf{I}_{uwvx} + \mathbf{I}'_{uwvx} + \mathbf{J}_{uwvx} + \mathbf{J}'_{uwvx} - \mathbf{J}_{uwxv} - \mathbf{J}'_{uwxv}, \tag{12}$$

with

$$\mathbf{I}_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C^*_{\gamma u} C^*_{\delta w} \langle \alpha\beta || \gamma\delta \rangle_a C_{\alpha v} C_{\beta x}, \tag{13}$$

$$\mathbf{J}_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C^*_{\gamma u} C'^*_{\delta w} \langle \alpha\beta || \gamma\delta \rangle C_{\alpha v} C'_{\beta x}, \tag{14}$$

$$\mathbf{I}'_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C'^*_{\gamma u} C'^*_{\delta w} \langle \alpha\beta || \gamma\delta \rangle_a C'_{\alpha v} C'_{\beta x}, \tag{15}$$

$$\mathbf{J}'_{uw,vx} = \sum_{\alpha\beta\gamma\delta} C'^*_{\gamma u} C^*_{\delta w} \langle \alpha\beta || \gamma\delta \rangle C'_{\alpha v} C_{\beta x} \tag{16}$$

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

Matrix $\mathbf{L}_M$ with its elements defined by relations (11) and (12) 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 $\langle \alpha\beta || \gamma\delta \rangle$.

The eigenvalues of $\mathbf{L}_M$ characterize the kind of local extremum point $\{C_{\mu l}, C'_{\mu l}\}$ determined by eqs. (6) and (7). (see paper I.)

3. Instability matrices

Matrix (8) corresponds to the instability matrix of the TSW (torsional spin wave) solution in the Fukutome nomenclature [3,4]. Since for the other classes of HF-solutions, the MSOs used are special cases of MSOs given by (3), it is natural to think that, in principle, we can derive instability matrices for each kind of HF-solution from (8) imposing restrictions on the LCAO-MO coefficients.

In fact, to determine theses particular instability matrices we have achieved a direct two-step procedure: Firstly we have defined an unitary similarity transformation. This is done using elements of the permutation group $S_N = \{\Omega\}$ in matrix form $[\mathbf{\Omega}]$. Next, we have imposed on the LCAO coefficients conditions according to the class of HF solution. The unitary similarity transformation does not change the eigenvalues of the Hermitian matrix $\mathbf{L}_M$ given by (8) and allows us to write the

blocks $\mathbf{L}_M^a$ $(a = 1, 2)$ in an alternative and convenient way to compare our instability matrices with Fukutome results. Specifically, we obtain that $\mathbf{L}_M'^a = [\mathbf{\Omega}^a]\mathbf{L}_M^a[\mathbf{\Omega}^a]^{-1}$ can be written as [7]

$$\mathbf{L}_M'^a = \begin{pmatrix} OOOO & OEOE & OOOE & OEOO \\ EOEO & EEEE & EOEE & EEEO \\ OOEO & OEEE & OOEE & OEEO \\ EOOO & EEOE & EOOE & EEOO \end{pmatrix}, \tag{17}$$

where $OOEE$, for example, designates a submatrix of $\mathbf{L}_M'^a$ whose elements have for its four $uvwx$-indices Odd, Odd, Even, Even numbers, respectively. We will denote in the block $\mathbf{L}_M'^1$ each submatrix whose elements are arranged in the form (17) by a capital letter, and each submatrix in $\mathbf{L}_M'^2$ by the corresponding small letter, that is,

$$\mathbf{L}_M'^1 = \begin{pmatrix} \mathbf{A} & \mathbf{B} & \mathbf{C} & \mathbf{D} \\ \mathbf{F} & \mathbf{G} & \mathbf{H} & \mathbf{I} \\ \mathbf{J} & \mathbf{K} & \mathbf{L} & \mathbf{M} \\ \mathbf{N} & \mathbf{O} & \mathbf{P} & \mathbf{Q} \end{pmatrix}, \tag{18}$$

$$\mathbf{L}_M'^2 = \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} & \mathbf{d} \\ \mathbf{f} & \mathbf{g} & \mathbf{h} & \mathbf{i} \\ \mathbf{j} & \mathbf{k} & \mathbf{l} & \mathbf{m} \\ \mathbf{n} & \mathbf{o} & \mathbf{p} & \mathbf{q} \end{pmatrix}. \tag{19}$$

Thus, the instability matrices for each class of HF solution are obtained as follows:

(a) *Torsional spin density wave (TSDW) solutions*

In this case φ_k and φ_k' in eq. (3) are real functions [8]. In consequence, we have real LCAO-MO coefficients. Thus, from eqs. (11) and (12) we have $\mathbf{L}_M^a = (\mathbf{L}_M^a)^*$, $a = 1, 2$. Further we can factorize the eigenvalue problem associated with $\mathbf{L}_M$ and instead consider eigenvalue problems associated with the instability matrices

$$\mathbf{L}_M(M_+) = \mathbf{L}_M'^1 + \mathbf{L}_M'^2,$$
$$\mathbf{L}_M(M_-) = \mathbf{L}_M'^1 - \mathbf{L}_M'^2.$$

$\mathbf{L}_M(M_+)$ and $\mathbf{L}_M(M_-)$ are the instability matrices for the TSDW solutions. The symbols in parentheses (M_+ and M_-, in this case) indicate the corresponding Fukutome symmetry classification for the instability matrix we have obtained.

(b) *Torsional spin current wave (TSCW) solutions*

This class of HF solutions refers to systems with an even number of electrons. It has pairs of MSOs in the form (α and β spin eigenfunctions)

$$\psi_1 = \varphi\alpha + \varphi'^*\beta\,,$$

$$\psi_2 = -\varphi'\alpha + \varphi^*\beta\,.$$

Therefore, $\mathbf{C}_{2i} = -\mathbf{C}'^*_{2i-1}$, $\mathbf{C}'_{2i} = \mathbf{C}^*_{2i-1}$, $i = 1, 2, \ldots, m/2$. Using these conditions in relations (11) and (12) we verify that $\mathbf{F} = \mathbf{B}^*$, $\mathbf{G} = \mathbf{A}^*$, $\mathbf{H} = \mathbf{D}^*$, $\mathbf{I} = \mathbf{C}^*$, $\mathbf{M} = \mathbf{K}^*$, $\mathbf{O} = \mathbf{J}^*$, $\mathbf{P} = \mathbf{N}^*$, $\mathbf{q} = \mathbf{I}^*$, $\mathbf{f} = \mathbf{b}^*$, $\mathbf{g} = \mathbf{a}^*$, $\mathbf{h} = \mathbf{d}^*$, $\mathbf{i} = \mathbf{c}^*$, $\mathbf{n} = \mathbf{k}^*$, $\mathbf{o} = \mathbf{j}^*$, $\mathbf{p} = \mathbf{m}^*$, and $\mathbf{q} = \mathbf{l}^*$. Hence the instability matrix $\mathbf{L}_M$ can be written as

$$\mathbf{L}_M = \begin{pmatrix} \mathbf{L}''^1_M & \mathbf{L}''^2_M \\ \mathbf{L}''^2_M & \mathbf{L}''^1_M \end{pmatrix}, \tag{20}$$

where $\mathbf{L}''^a_M$ are obtained from eqs. (18) and (19) and permutations of rows and columns, i.e.

$$\mathbf{L}''^1_M = \begin{pmatrix} \mathbf{B} & \mathbf{A} & \mathbf{D} & \mathbf{C} \\ \mathbf{A}^* & \mathbf{B}^* & \mathbf{C}^* & \mathbf{D}^* \\ \mathbf{K} & \mathbf{J} & \mathbf{M} & \mathbf{L} \\ \mathbf{J}^* & \mathbf{K}^* & \mathbf{L}^* & \mathbf{M}^* \end{pmatrix} \tag{21}$$

and

$$\mathbf{L}''^2_M = \begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} & \mathbf{d} \\ \mathbf{b}^* & \mathbf{a}^* & \mathbf{d}^* & \mathbf{c}^* \\ \mathbf{j} & \mathbf{k} & \mathbf{l} & \mathbf{m} \\ \mathbf{k}^* & \mathbf{j}^* & \mathbf{m}^* & \mathbf{l}^* \end{pmatrix}. \tag{22}$$

The eigenvalue problem associated with matrix (20) factorizes also in this case, and we obtain for TSCW solutions the instability matrices

$$\mathbf{L}_M(T_+) = \mathbf{L}''^1_M + \mathbf{L}''^2_M\,,$$

$$\mathbf{L}_M(T_-) = \mathbf{L}''^1_M - \mathbf{L}''^2_M.$$

(c) *Axial spin wave (ASW) solutions*

This class has MSOs given by

$$\psi_1 = \varphi\alpha,$$

$$\psi_2 = \varphi'\beta,$$

or correspondingly,

$$\mathbf{C}'_{2k-1} = \mathbf{0},$$

$$\mathbf{C}_{2k} = \mathbf{0}.$$

With these conditions, we obtain

$$\mathbf{L}_M(A_+) = \begin{pmatrix} \mathbf{A} & \mathbf{B} & \mathbf{a} & \mathbf{b} \\ \mathbf{F} & \mathbf{G} & \mathbf{f} & \mathbf{g} \\ \mathbf{a}^* & \mathbf{b}^* & \mathbf{A}^* & \mathbf{B}^* \\ \mathbf{f}^* & \mathbf{g}^* & \mathbf{F}^* & \mathbf{G}^* \end{pmatrix} \tag{23}$$

and

$$\mathbf{L}_M(A_-) = \begin{pmatrix} \mathbf{I} & \mathbf{m} \\ \mathbf{p}^* & \mathbf{Q}^* \end{pmatrix}. \tag{24}$$

(d) *Axial spin density wave (ASDW) solutions*

The instability matrices of this class are easily obtained from the ASW matrices. The additional restriction on the MSOs is that the MSOs must be real. Then, we have

$$\mathbf{L}_M(A_-M) = \begin{pmatrix} \mathbf{I} & \mathbf{m} \\ \mathbf{p} & \mathbf{Q} \end{pmatrix} \tag{25}$$

and

$$\mathbf{L}_M(A_+M_\pm) = \begin{pmatrix} (\mathbf{A} \pm \mathbf{a}) & (\mathbf{B} \pm \mathbf{b}) \\ (\mathbf{F} \pm \mathbf{f}) & (\mathbf{G} \pm \mathbf{g}) \end{pmatrix}. \tag{26}$$

(e) *Axial spin current wave (ASCW) solutions*

We add to the restrictions of the ASW class, the following condition

$$\mathbf{C}'_{2k} = \mathbf{C}^*_{2k-1}. \tag{27}$$

Thus, we verify the relations: $\mathbf{G} = \mathbf{A}^*$, $\mathbf{F} = \mathbf{B}^*$, $\mathbf{g} = \mathbf{a}^*$, $\mathbf{f} = \mathbf{b}^*$, $\mathbf{Q} = \mathbf{L}^*$, and $\mathbf{p} = \mathbf{m}^*$. Therefore, the instability matrices become

$$\mathbf{L}_M(A_-T_\pm) = \mathbf{L} \pm \mathbf{m} \tag{28}$$

and

$$\mathbf{L}_M(A_+T_\pm) = \begin{pmatrix} (\mathbf{A} \pm \mathbf{b}) & (\mathbf{B} \pm \mathbf{a}) \\ (\mathbf{B}^* \pm \mathbf{a}^*) & (\mathbf{A}^* \pm \mathbf{b}^*) \end{pmatrix}. \tag{29}$$

(f) *Charge current wave (CCW) solutions*

This class of closed shell solutions has the additional restriction on the ASW class given by

$$\mathbf{C}'_{2k} = \mathbf{C}_{2k-1}. \tag{30}$$

It follows that $\mathbf{A} = \mathbf{G}$, $\mathbf{B} = \mathbf{F}$, $\mathbf{a} = \mathbf{g}$, $\mathbf{b} = \mathbf{f}$, $\mathbf{L} = \mathbf{Q}$, and $\mathbf{m} = \mathbf{p}$. Hence, we arrive at

$$\mathbf{L}_M(^1S) = \begin{pmatrix} (\mathbf{A}+\mathbf{B}) & (\mathbf{a}+\mathbf{b}) \\ (\mathbf{a}^*+\mathbf{b}^*) & (\mathbf{A}^*+\mathbf{B}^*) \end{pmatrix} \tag{31}$$

and

$$\mathbf{L}_M(^3S) = \begin{pmatrix} \mathbf{L} & \mathbf{m} \\ \mathbf{m}^* & \mathbf{L}^* \end{pmatrix}. \tag{32}$$

(g) *Time-reversal invariant closed shell (TICS) solutions*

This class of HF solutions, closed shell with real MSOs, is the most used class in molecular calculations. The corresponding instability matrices are obtained from the CCW matrices through the condition of the MSOs being real.

We have that $\mathbf{B} = \mathbf{b}$. Then, the instability matrices become

$$\mathbf{L}_M(^1ST_+) = \mathbf{A} + 2\mathbf{B} + \mathbf{a}, \tag{33}$$

$$\mathbf{L}_M(^1ST_-) = \mathbf{A} - \mathbf{a}, \tag{34}$$

$$\mathbf{L}_M(^3ST_+) = \mathbf{L} - \mathbf{m}, \tag{35}$$

$$\mathbf{L}_M(^3ST_-) = \mathbf{L} + \mathbf{m}. \tag{36}$$

The instability matrices $\mathbf{L}_M(^1ST_+)$ and $\mathbf{L}_M(^3ST_-)$ correspond to the well known singlet and triplet instability in the Cizek–Paldus classification [9]. $\mathbf{L}_M(^1ST_+)$ and $\mathbf{L}_M(^3ST_-)$ were classified by Chambaud et al. [10] as non-real instabilities. Finally, we could classify the possible transformed instability matrices by the irreducible representations of S_N. Nevertheless, we believe that the actual classification is already quite good.

4. Discussion and concluding remarks

In the previous 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 analyzed as a polynomial function of the LCAO coefficients, i.e., as a real-valued function $E(X)$ 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.

In order to apply our development, however, it is necessary to know the different instability matrices for each class of HF solutions and to compare these matrices with those determined by others methods. This might look like a difficult task since the MMF is general and does not use symmetry considerations. Here we have demonstrated that using unitary similarity transformations applied to $\mathbf{L}_M$ and

imposing conditions on the LCAO coefficients according to the class of HF solution we obtained all the known instability matrices from our fundamental matrix $\mathbf{L}_M$. These matrices are expressed in terms of LCAO coefficients, therefore they are of straightforward application on numerical calculations. The eigenvalues of the instability matrices characterize the extremum points (the solutions of the HF calculations) as maximum, minimum or saddle points [1]. This characterization may guide the search for better solutions or the absolute minimum.

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