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Self-consistent molecular orbital methods. XVIII. Constraints and stability in Hartree-Fock theory

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Constraints that may be applied to the spin orbitals used in Hartree-Fock theory are classified and discussed. Once a constrained stationary wavefunction has been obtained by a self-consistent procedure, it may be tested for stability both internally (with constraints remaining) and externally (with some constraints removed). Methods for carrying out these tests are presented. In addition, a general technique is described for further energy minimization following detection of an instability.

I. INTRODUCTION

Hartree-Fock orbital theory is concerned with the determination of antisymmetrized-product (single-determinant) wavefunctions for an n -electron system,

$$\Psi = A \det(\chi_1 \chi_2 \dots \chi_n). \quad (1)$$

In this equation χ_j ($j=1, 2, \dots, n$) is a function of the coordinates of a single electron (Cartesian coordinates \mathbf{r} and spin coordinate ξ) and A is a normalization constant. The χ_i are commonly termed spin orbitals. From a wavefunction such as (1), an expectation value for the energy \mathcal{E} can be obtained

$$\mathcal{E}(\Psi) = \int \dots \int \Psi^* \mathcal{H} \Psi d\tau_1 \dots d\tau_n, \quad (2)$$

where \mathcal{H} is the nonrelativistic Hamiltonian for the system. Integration is over all coordinates of all electrons. The energy $\mathcal{E}(\Psi)$ is an upper bound for the energy of the corresponding electronic ground state. The Hartree-Fock procedure is then to determine an optimum single-determinant wavefunction by variation of the χ_i to minimize the energy $\mathcal{E}(\Psi)$.

In practice, complete variation of the spin orbitals $\{\chi\}$ is rarely attempted. Usually, a number of constraints is imposed and variation of Ψ is carried out within a more restricted space. Examples of such constraints are representation of each χ_i as a product of a function of the Cartesian coordinates with a function of the spin coordinates, restriction to real functions, coincidence of some spin orbitals, and linear expansion in terms of a finite set of basis functions. Given the nature of such a constrained function space, common practice is to seek stationary values of the energy expression (2), usually by an iterative method. This is the self-consistent field (SCF) procedure. It ensures that infinitesimal variation of the χ_i within the constrained space leads to zero first-order changes in the energy $\mathcal{E}(\Psi)$.

To establish that $\mathcal{E}(\Psi)$ is a local minimum within a constrained $\{\chi\}$ space, it is necessary to examine its second-order variation and to show that it is always positive. The original theory for this was given by Thouless,¹ and there has been a number of more recent developments.²⁻⁶ Once a local minimum is found within a constrained space, one may then consider the consequences of removing one or more of the constraints. There are three possibilities. The first is,

that the Ψ already determined still corresponds to a local minimum of $\mathcal{E}(\Psi)$ even in the less constrained space. Secondly, $\mathcal{E}(\Psi)$ may still be stationary in the less constrained space, but no longer be a minimum. Thirdly, $\mathcal{E}(\Psi)$ may no longer be even stationary. In the second and third eventualities, a further search for a local minimum is indicated. Ostlund⁷ has studied such behavior of $\mathcal{E}(\Psi)$ under various derestrictions, starting with a real single determinant wavefunction constructed from doubly-occupied molecular orbitals.

The present paper has three main aims. In the first place, we shall classify systematically the various spin-orbital constraints that may be imposed and discuss their physical implications. The second objective is to study second order stability conditions, both for variations within the constrained spaces (internal stability) and outside (external stability). Finally we shall discuss practical techniques for stability studies and subsequent energy minimizations.

II. CLASSIFICATION OF SPIN ORBITAL CONSTRAINTS

The completely unconstrained spin orbital is a complex function $\chi(\mathbf{r}, \xi)$ of the Cartesian coordinates \mathbf{r} and spin coordinate ξ of a single electron. When inserted in the determinantal wavefunction (1), it is generally taken to satisfy the conditions

$$\int \chi_j^* \chi_k d\tau = \delta_{jk}, \quad (3)$$

where δ_{jk} is the Kronecker delta. However, because of the properties of the determinant, this condition does not imply any constraint on the full wavefunction Ψ .

If, following common practice, we expand the functions in spin space over the two spin basis functions $\alpha(\xi)$ and $\beta(\xi)$, which are eigenfunctions of the spin component operator s_z corresponding, respectively, to eigenvalues of $+\frac{1}{2}$ and $-\frac{1}{2}$, then the general χ_j has the form

$$\chi_j(\mathbf{r}, \xi) = \psi_j^\alpha(\mathbf{r})\alpha(\xi) + \psi_j^\beta(\mathbf{r})\beta(\xi), \quad (4)$$

where ψ_j^α , ψ_j^β are orbitals which are functions of the Cartesian coordinates \mathbf{r} only. In general ψ_j^α and ψ_j^β will be complex and can be written in real and imaginary parts,

$$\begin{aligned} \psi_j^\alpha &= \text{Re}(\psi_j^\alpha) + i \text{Im}(\psi_j^\alpha), \\ \psi_j^\beta &= \text{Re}(\psi_j^\beta) + i \text{Im}(\psi_j^\beta). \end{aligned} \quad (5)$$

Thus the general spin orbitals can be completely specified by four real functions of \mathbf{r} . If we expand χ_j in terms of a set of N suitable real basis functions of the Cartesian coordinates \mathbf{r} , $\{\varphi_\mu(\mathbf{r})\}_{\mu=1}^N$, we obtain

$$\chi_j(\mathbf{r}, \xi) = \sum_{\mu=1}^N [c_{\mu j}^\alpha \varphi_\mu(\mathbf{r}) \alpha(\xi) + c_{\mu j}^\beta \varphi_\mu(\mathbf{r}) \beta(\xi)], \quad (6)$$

where $c_{\mu j}^\alpha$ and $c_{\mu j}^\beta$ are complex constants. Hence, within this more constrained space, specification of this general spin orbital χ_j requires $4N$ real numbers. We shall refer to the theory in which the full expression (6) is used as *general Hartree-Fock theory* (GHF).

We now turn to the constraints that are commonly imposed on the spin orbitals, leading to more restricted forms of Hartree-Fock theory.

A. Product spin orbitals

The first constraint, almost universally used, is the assumption that each spin orbital χ_j has the form either $\psi_j^\alpha(\mathbf{r})\alpha(\xi)$ or $\psi_j^\beta(\mathbf{r})\beta(\xi)$, but not a combination of both. χ_j is then a *product spin orbital* and the Cartesian part, ψ_j^α or ψ_j^β , is usually described as a molecular orbital. The α orbitals and β orbitals, however, are treated as independent complex functions. This version of the theory is frequently termed *spin-unrestricted Hartree-Fock theory* (UHF). With a basis set $\{\varphi\}$, each product spin orbital χ_j is determined by N complex coefficients $c_{\mu j}^\alpha$ or $c_{\mu j}^\beta$. One important property of a UHF wavefunction is that it is an eigenfunction of the total spin-component operator

$$S_z = \sum_p s_z(p), \quad (7)$$

where the sum is over all electrons.

B. Real spin orbitals

The next constraint used to simplify the theory is the restriction to real orbitals ψ^α or ψ^β . This level of theory (real UHF) requires only N real coefficients ($c_{\mu j}^\alpha$ or $c_{\mu j}^\beta$) for each spin orbital.

C. Spin-restricted orbitals

A further important constraint often used relates the orbitals of different spin ψ^α and ψ^β . If the numbers of occupied α and β orbitals are n_α and n_β ($n_\alpha \geq n_\beta$), then we may constrain n_β of the α orbitals to be identical with the β orbitals. These n_β orbitals are then "doubly occupied." The remaining $(n_\alpha - n_\beta)$ α orbitals are "singly occupied." This version is usually described as *spin-restricted Hartree-Fock theory* (RHF). The corresponding total wave function is then additionally an eigenfunction of the total spin operator

$$S^2 = \left[\sum_p s(p) \right]^2. \quad (8)$$

RHF theory may be used in complex form (complex RHF) or with the constraint of real orbitals. For $n_\alpha = n_\beta = \frac{1}{2}n$, this leads to a set of doubly occupied molecular orbitals representing the familiar "closed-shell" approximation to a singlet molecular electronic ground state.

These various constraints are introduced partly to facilitate application of the theory and partly to make the resulting determinantal function have certain features in common with the exact wavefunction. With the commonly used spin-independent many-electron Hamiltonian, the exact wavefunction may be chosen to be real, is an eigenfunction of S^2 and may be chosen to be an eigenfunction of the total spin component operator S_z . However, the single determinant with lowest electronic energy \mathcal{E} [Eq. (2)] does not necessarily satisfy these conditions⁸ (except for one-electron systems where the exact wavefunction is a single spin orbital). The imposition of constraints may therefore raise the computed energy, taking it further from the exact value. It may turn out, however, that unconstrained variation of the spin orbitals leads to no lower energy \mathcal{E} than a constrained theory. Nevertheless, it is generally desirable to test whether a wavefunction can be altered to yield a lower energy either by further variation within the constrained space or by removal of some of the constraints. This is the primary task of Hartree-Fock stability studies.

III. STABILITY CONDITIONS

The various spin orbital constraints described in the previous section can be applied or removed in various orders. We shall not consider all possibilities and limit ourselves to the removal of constraints in the steps shown in Fig. 1.

In this section we examine conditions for internal and external stability at each step, leading to results summarized in Table I. We adopt a notation close to that of Čížek and Paldus,⁶ who derived general conditions for the stability of a GHF wavefunction. Although only the spin orbitals χ_1, \dots, χ_n are used to construct the determinantal wavefunction (1), it is convenient to complete this set with the remaining eigenfunctions of the Fock Hamiltonian, $\chi_{n+1}, \dots, \chi_{2N}$, called the *virtual* spin orbitals. With this full set of spin orbitals, we obtain a set of orthonormal determinants by replacing all possible combinations of occupied spin orbitals χ_i ($1 \leq i \leq n$) with all possible combinations of virtual spin orbitals χ_a ($n < a \leq 2N$). This set of determinantal functions can then be used to expand the general determinantal wavefunction $\tilde{\Psi}$ in the vicinity of a given ground wavefunction Ψ_0 ,

$$\tilde{\Psi} = \Psi_0 + \sum_i \sum_a^{\text{occ}} \sum_a^{\text{virt}} D_{i \rightarrow a} \Psi_{i \rightarrow a} + \sum_i \sum_a^{\text{occ}} \sum_j^{\text{occ}} \sum_b^{\text{virt}} D_{i \rightarrow a} D_{j \rightarrow b} \times \Psi_{i \rightarrow a, j \rightarrow b} + \dots \quad (9)$$

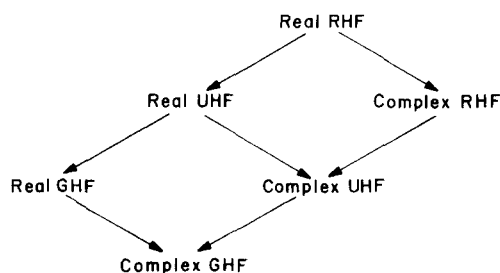


FIG. 1. Release of constraints in Hartree-Fock theory.

TABLE I. Matrices required to have positive semidefinite character as a necessary condition for stability of self-consistent solution of type X in the space of type Y .

$X \backslash Y$	Real RHF ^a	Complex RHF	Real UHF	Complex UHF	Real GHF	Complex GHF
Real RHF ^a	${}^1\mathbf{A}' + {}^1\mathbf{B}'$	${}^1\mathbf{A}' - {}^1\mathbf{B}'$	${}^3\mathbf{A}' + {}^3\mathbf{B}'$			
Complex RHF		${}^1\mathbf{H}'$		${}^3\mathbf{H}'$		
Real UHF			$\mathbf{A}' + \mathbf{B}'$	$\mathbf{A}' - \mathbf{B}'$	$\mathbf{A}'' + \mathbf{B}''$	
Complex UHF				\mathbf{H}'		\mathbf{H}''
Real GHF					$\mathbf{A} + \mathbf{B}$	$\mathbf{A} - \mathbf{B}$
Complex GHF						\mathbf{H}

^aSinglet closed shell case ($n_\alpha = n_\beta$) only.

$\Psi_{i \rightarrow a}$ denoting the replacement of orbital χ_i by χ_a . Suppose the ground wavefunction Ψ_0 is given by (1). Then

$$\Psi_{i \rightarrow a} = \det(\chi_1 \chi_2 \dots \chi_a \dots \chi_n) \quad (10)$$

where χ_a replaces χ_i , and

$$\Psi_{i \rightarrow a, j \rightarrow b} = \det(\chi_1 \chi_2 \dots \chi_a \dots \chi_b \dots \chi_n) \quad (11)$$

where χ_i and χ_j are replaced by χ_a and χ_b , respectively. Clearly $\Psi_{i \rightarrow a, j \rightarrow b}$ is not defined, or vanishes, if either $\chi_i = \chi_j$ or $\chi_a = \chi_b$, or both. To simplify the notation, we denote each replacement, e.g., $i \rightarrow a$, by a single letter, e.g., s and the coefficients $D_{i \rightarrow a}$ by D_s . Equation (9) then becomes

$$\tilde{\Psi} = \Psi_0 + \sum_s D_s \Psi_s + \sum_s \sum_t D_s D_t \Psi_{st} + \dots \quad (12)$$

Note that $\tilde{\Psi}$ is not normalized.

Čížek and Paldus⁸ calculate the electronic energy \mathcal{E} for a $\tilde{\Psi}$ according to (12) to second order. If Ψ_0 already gives a stationary energy (and so is self-consistent), the first order contribution vanishes by virtue of the Brillouin theorem.⁹ The second order contribution is then

$$\mathcal{E}_2 = \sum_{st} \{ D_s^* D_t \langle s | \mathcal{Q} | t \rangle + \frac{1}{2} D_s D_t \langle 0 | \mathcal{Q} | st \rangle + \frac{1}{2} D_s^* D_t^* \langle st | \mathcal{Q} | 0 \rangle \} \quad (13)$$

where

$$\mathcal{Q} = \mathcal{H} - \langle 0 | \mathcal{H} | 0 \rangle \quad (14)$$

and the $\langle \rangle$ notation implies integration over all coordinates of all electrons. For the nonrelativistic Schrödinger Hamiltonian, evaluation of the matrix elements in Eq. (13) gives ($s \equiv i \rightarrow a$, $t \equiv j \rightarrow b$),

$$A_{st} \equiv \langle s | \mathcal{Q} | t \rangle = (\epsilon_a - \epsilon_i) \delta_{st} + \langle ij | ib \rangle, \quad (15)$$

$$B_{st} \equiv \langle st | \mathcal{Q} | 0 \rangle = \langle ab | ij \rangle. \quad (16)$$

Here, ϵ_i and ϵ_a are eigenvalues of the one-electron Fock operator and the notation for the two-electron integrals is

$$\langle ab | ij \rangle = \iint \chi_a^*(1) \chi_b^*(2) (1/r_{12}) [\chi_i(1) \chi_j(2) - \chi_j(1) \chi_i(2)] d\tau_1 d\tau_2. \quad (17)$$

Here integration is over Cartesian and spin coordinates. Note that \mathbf{A} is Hermitian and \mathbf{B} is symmetric.

Čížek and Paldus⁵ then write Eq. (13) in matrix form

$$\mathcal{E}_2 = \frac{1}{2} \begin{pmatrix} \mathbf{D} \\ \mathbf{D}^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{D} \\ \mathbf{D}^* \end{pmatrix}, \quad (18)$$

where \mathbf{D}^* and \mathbf{D}^\dagger are the complex and Hermitian conjugate of \mathbf{D} , respectively. It follows that the matrix \mathbf{H} , given by

$$\mathbf{H} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \quad (19)$$

must be positive semidefinite as a necessary condition for stability. This analysis applies to the completely general GHF wavefunction. If Ψ_0 involves a resultant electron spin, the matrix \mathbf{H} will have zero eigenvalues, since direction of spin quantization is indeterminate. Only strictly negative eigenvalues imply instability.

We may next apply a similar analysis for a *real* GHF wavefunction. The spin orbitals will then have the form (6) with real coefficients $c_{\mu j}^\alpha$ and $c_{\mu j}^\beta$, the matrices \mathbf{A} and \mathbf{B} become real and consequently Eq. (18) may be rearranged in the form

$$\mathcal{E}_2 = \frac{1}{4} [(\mathbf{D} + \mathbf{D}^*)^\dagger (\mathbf{A} + \mathbf{B}) (\mathbf{D} + \mathbf{D}^*) + (\mathbf{D} - \mathbf{D}^*)^\dagger (\mathbf{A} - \mathbf{B}) (\mathbf{D} - \mathbf{D}^*)]. \quad (20)$$

If we consider only internal stability, that is stability under perturbations which keeps the spin orbitals real, then only displacements with $\mathbf{D} = \mathbf{D}^*$ are appropriate. Consequently, a necessary condition for *internal* stability is positive semidefinite character for $\mathbf{A} + \mathbf{B}$. However, if the constraint of being real is removed, the spin orbitals can acquire imaginary parts by displacements with $\mathbf{D} = -\mathbf{D}^*$. Thus for *external* stability relative to complex spin orbitals, a necessary condition is positive semidefinite character for $\mathbf{A} - \mathbf{B}$.

Next we wish to apply the same analysis to obtain stability conditions for the *complex* UHF wavefunction, where each spin orbital is a product $\psi_j^\alpha(\mathbf{r})\alpha(\xi)$ or $\psi_j^\beta(\mathbf{r})\beta(\xi)$. If Ψ_0 is a stationary solution within this constrained space, the replacements s may be classified as

(i) spin-conserved ($\alpha \rightarrow \alpha$, $\beta \rightarrow \beta$)

or

(ii) spin-unconserved ($\alpha \rightarrow \beta$, $\beta \rightarrow \alpha$).

From Eq. (9) we see that spin-conserved replacements in the determinant leave the α and β spin spaces uncoupled, whereas spin-unconserved replacements introduce in general a coupling between the two spin spaces.

The matrices **A** and **B** factorize into spin-conserved parts (**A'**, **B'**) and spin-unconserved parts (**A''**, **B''**) as follows from Eqs. (15) and (16) by integration over the spin coordinates. The matrix elements for the *spin-conserved* replacements with $s=t=\alpha-\alpha$ or $s=t=\beta-\beta$ are

$$A'_{st} = (\epsilon_a - \epsilon_i) \delta_{st} + (aj | r_{12}^{-1} | ib) - (aj | r_{12}^{-1} | bi), \quad (21a)$$

$$B'_{st} = (ab | r_{12}^{-1} | ij) - (ab | r_{12}^{-1} | ji). \quad (21b)$$

With $s=\alpha-\alpha$, $t=\beta-\beta$ or $s=\beta-\beta$, $t=\alpha-\alpha$

$$A'_{st} = (aj | r_{12}^{-1} | ib), \quad (22a)$$

$$B'_{st} = (ab | r_{12}^{-1} | ij). \quad (22b)$$

For real orbitals we then obtain $A'_{st} = B'_{st}$, since $\chi_i = \chi_i^*$ and $\chi_a = \chi_a^*$. The notation for the two-electron integral used here is defined as

$$(ij | r_{12}^{-1} | kl) = \iint \psi_i^*(1) \psi_j^*(2) r_{12}^{-1} \psi_k(1) \psi_l(2) d\mathbf{r}_1 d\mathbf{r}_2,$$

the integration now being only over the Cartesian coordinates **r** of two electrons. The *spin-unconserved* replacements result in the following matrix elements:

With $s=t=\alpha-\beta$ or $s=t=\beta-\alpha$

$$A''_{st} = (\epsilon_a - \epsilon_i) \delta_{st} - (aj | r_{12}^{-1} | bi) \quad (23a)$$

$$B''_{st} = 0, \quad (23b)$$

and finally, for $s=\alpha-\beta$, $t=\beta-\alpha$ or $s=\beta-\alpha$, $t=\alpha-\beta$

$$A''_{st} = 0, \quad (24a)$$

$$B''_{st} = - (ab | r_{12}^{-1} | ji). \quad (24b)$$

Thus the **A''** and **B''** matrices have the structure depicted in Fig. 2. A necessary condition for internal stability of Ψ_0 is therefore the positive semidefinite character of the matrix

$$\mathbf{H}' = \begin{pmatrix} \mathbf{A}' & \mathbf{B}' \\ (\mathbf{B}')^* & (\mathbf{A}')^* \end{pmatrix}. \quad (25)$$

Correspondingly, external stability can be tested by examining the matrix

$$\mathbf{H}'' = \begin{pmatrix} \mathbf{A}'' & \mathbf{B}'' \\ (\mathbf{B}'')^* & (\mathbf{A}'')^* \end{pmatrix}. \quad (26)$$

If $n_\alpha \neq n_\beta$, so that there is resultant electron spin, **H''**

		$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$
\mathbf{A}'' :	$\alpha \rightarrow \beta$	\times	0
	$\beta \rightarrow \alpha$	0	\times

		$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$
\mathbf{B}'' :	$\alpha \rightarrow \beta$	0	\times
	$\beta \rightarrow \alpha$	\times	0

FIG. 2. Blockform of matrices **A''** and **B''**.

will have zero eigenvalues corresponding to changing the direction of spin-quantization without change of energy.

The next step is to test a *real* UHF stationary solution Ψ_0 , both internally (retaining real functions) and also externally with respect to both complex perturbations (complex UHF) and perturbations leading to real GHF spin orbitals. Let us postpone consideration of the latter and restrict ourselves to *spin-conserved* replacements. Since Ψ_0 is real, both matrices **A'** and **B'** are real and we obtain

$$\mathcal{E}_2 = \frac{1}{2} \begin{pmatrix} \mathbf{D}' \\ (\mathbf{D}')^* \end{pmatrix}^\dagger \begin{pmatrix} \mathbf{A}' & \mathbf{B}' \\ \mathbf{B}' & \mathbf{A}' \end{pmatrix} \begin{pmatrix} \mathbf{D}' \\ (\mathbf{D}')^* \end{pmatrix}. \quad (27)$$

This may be rewritten as

$$\mathcal{E}_2 = \frac{1}{4} \{ [\mathbf{D}' + (\mathbf{D}')^*]^\dagger (\mathbf{A}' + \mathbf{B}') [\mathbf{D}' + (\mathbf{D}')^*] + [\mathbf{D}' - (\mathbf{D}')^*]^\dagger \times (\mathbf{A}' - \mathbf{B}') [\mathbf{D}' - (\mathbf{D}')^*] \}. \quad (28)$$

It follows that a necessary condition for internal stability of a real UHF wavefunction is that the matrix **A' + B'** is positive semidefinite. The corresponding necessary condition for external stability relative to the complex UHF space is that **A' - B'** is positive semidefinite. Equations (21a)–(21b) provide the following matrix elements, for $s=t=\alpha-\alpha$:

$$A'_{st} + B'_{st} = (\epsilon_a - \epsilon_i) \delta_{st} + 2(aj | r_{12}^{-1} | ib) - (aj | r_{12}^{-1} | bi) - (ab | r_{12}^{-1} | ji), \quad (29a)$$

$$A'_{st} - B'_{st} = (\epsilon_a - \epsilon_i) \delta_{st} - (aj | r_{12}^{-1} | bi) + (ab | r_{12}^{-1} | ji), \quad (29b)$$

and for $s=\alpha-\alpha$, $t=\beta-\beta$ or $s=\beta-\beta$, $t=\alpha-\alpha$

$$A'_{st} + B'_{st} = 2(aj | r_{12}^{-1} | ib), \quad (30a)$$

$$A'_{st} - B'_{st} = 0. \quad (30b)$$

Note that the matrix **A' - B'** factorizes into a pure $\alpha-\alpha$ and a pure $\beta-\beta$ block, thus simplifying the search for its lowest eigenvalue.

Turning to the *spin-unconserved* displacements **D''**, these lead to an energy change

$$\mathcal{E}_2 = \frac{1}{4} \{ [\mathbf{D}'' + (\mathbf{D}'')^*]^\dagger (\mathbf{A}'' + \mathbf{B}'') [\mathbf{D}'' + (\mathbf{D}'')^*] - [\mathbf{D}'' - (\mathbf{D}'')^*]^\dagger (\mathbf{A}'' - \mathbf{B}'') [\mathbf{D}'' - (\mathbf{D}'')^*] \}. \quad (31)$$

The first part of this expression corresponds to displacements to real GHF functions, while the second part mixes in imaginary components of the opposite spin virtual spin orbitals. The matrix elements for **A'' + B''** and **A'' - B''** are given by the Eqs. (23a) to (24b) under the assumption that all orbitals are real. For $s=t=\alpha-\beta$ or $s=t=\beta-\alpha$, we obtain

$$A''_{st} + B''_{st} = (\epsilon_a - \epsilon_i) \delta_{st} - (aj | r_{12}^{-1} | bi) = A''_{st} - B''_{st}, \quad (32)$$

and with $s=\alpha-\beta$, $t=\beta-\alpha$ or $s=\beta-\alpha$, $t=\alpha-\beta$

$$A''_{st} + B''_{st} = - (ab | r_{12}^{-1} | ji), \quad (33a)$$

$$A''_{st} - B''_{st} = (ab | r_{12}^{-1} | ji). \quad (33b)$$

Since **A'' + B''** and **A'' - B''** differ only by the sign of certain off-diagonal elements, their eigenvalues are the same. It follows that positive semidefinite character for **A'' + B''** is a necessary condition for external stability with respect to either kind of displacement.

It remains to consider the stability of the *spin-restricted* (RHF) wavefunctions, real or complex. If $n_\alpha \neq n_\beta$, so that there are both doubly and singly occupied molecular orbitals, the RHF wavefunctions are generally not even self-consistent in the UHF space so that no test for external stability is required. It is possible to develop a test for internal stability of such RHF functions, but this topic will not be pursued in this paper. We shall deal only with the stability problem for singlet closed shell RHF functions for which $n_\alpha = n_\beta$.

Consider first a *complex* RHF function in which molecular orbitals ψ_k ($1 \leq k \leq n_\alpha$) are doubly occupied and the remaining orbitals ψ_c ($n_\alpha < c \leq N$) are empty. If we are examining the stability of such a solution in the complex UHF space, only the spin-conserved replacements ($\alpha \rightarrow \alpha$, $\beta \rightarrow \beta$) need be considered, leading to the matrix \mathbf{H}' (Eq. (25)). To stay within the complex RHF space, the spin orbitals ψ_k^α and ψ_k^β must change their Cartesian parts by the same amount. If we define new quantities

$$\begin{aligned} {}^1D_{k-c} &= 2^{-1/2}[D_{k\alpha-c\alpha} + D_{k\beta-c\beta}], \\ {}^3D_{k-c} &= 2^{-1/2}[D_{k\alpha-c\alpha} - D_{k\beta-c\beta}], \end{aligned} \quad (34)$$

then ${}^1D_{k-c}$ corresponds to a displacement of the function within the complex RHF space (singlet mixing), while ${}^3D_{k-c}$ corresponds to displacement outside this space (triplet mixing). The matrices \mathbf{A}' , \mathbf{B}' , and \mathbf{H}' factorize into pairs (${}^1\mathbf{A}'$, ${}^3\mathbf{A}'$), (${}^1\mathbf{B}'$, ${}^3\mathbf{B}'$), and (${}^1\mathbf{H}'$, ${}^3\mathbf{H}'$) with elements

$$\begin{aligned} {}^1A'_{k-c, l-d} &= (\epsilon_c - \epsilon_k)\delta_{kl}\delta_{cd} + 2(c|l|r_{12}^{-1}|kd) - (c|l|r_{12}^{-1}|dk), \\ {}^3A'_{k-c, l-d} &= (\epsilon_c - \epsilon_k)\delta_{kl}\delta_{cd} - (c|l|r_{12}^{-1}|dk), \\ {}^1B'_{k-c, l-d} &= 2(cd|r_{12}^{-1}|kl) - (cd|r_{12}^{-1}|lk), \\ {}^3B'_{k-c, l-d} &= -(cd|r_{12}^{-1}|lk), \end{aligned} \quad (35)$$

and

$${}^{1,3}\mathbf{H}' = \begin{pmatrix} {}^{1,3}\mathbf{A}' & {}^{1,3}\mathbf{B}' \\ ({}^{1,3}\mathbf{B}')^* & ({}^{1,3}\mathbf{A}')^* \end{pmatrix}. \quad (36)$$

The necessary stability conditions for the complex RHF space are then positive semidefinite character for ${}^1\mathbf{H}'$ (internal stability) and for ${}^3\mathbf{H}'$ (external stability relative to complex UHF functions).

Finally, we consider the stability conditions for *real* RHF functions, again with the restriction to the singlet closed shell case ($n_\alpha = n_\beta$). This has been dealt with in detail by Ostlund.⁷ The necessary condition for internal stability is positive semidefinite character for ${}^1\mathbf{A}' + {}^1\mathbf{B}'$. For external stability the conditions are positive semidefinite character for ${}^1\mathbf{A}' - {}^1\mathbf{B}'$ (relative to complex RHF) and for ${}^3\mathbf{A}' + {}^3\mathbf{B}'$ (relative to real UHF).

It is useful to consider how the Hartree-Fock wavefunctions and energies can be followed through the removal of the constraints shown in Fig. 1 in the application to any particular problem. If it is desired to find a wavefunction and energy for the ground electronic state irrespective of its multiplicity, all constraints can be removed and the resulting energy will be an upper bound to the exact energy (that corresponding to the

solution of the Schrödinger equation). On the other hand, if it is desired to find a wavefunction and energy for the lowest state of given spin multiplicity, the only constraint that can be released is from real RHF to complex RHF. As previously noted, this release can lead to lower calculated energies under some circumstances.¹⁰ A general procedure, therefore, consists of the following steps:

- (1) Obtain a self-consistent solution at one level of Fig. 1.
- (2) Test this solution for internal stability.
- (3) If internally unstable, carry out a further search to find another solution of lower energy at the same level.
- (4) When an internally stable solution is found, test for external stability relative to a lower level in Fig. 1.
- (5) If external instability is found, proceed with a similar search procedure at this lower level.

It should be noted that a search following external instability does not lead to a unique new wavefunction. Thus, if a real wavefunction turns out to be unstable within the corresponding complex space, the optimized complex wavefunction and its complex conjugate will give the same electronic energy. Similarly, if an RHF wavefunction ($n_\alpha = n_\beta$) is unstable in the corresponding UHF space, two optimized wavefunctions differing only by interchange of α and β spin functions will also lead to the same energy.

IV. PRACTICAL HARTREE-FOCK PROCEDURES

In order to explore the performance of some of these levels of Hartree-Fock theory, we have developed a series of procedures to be associated with the Gaussian-70 computer program system.¹¹ These include self-consistent programs for real RHF, complex RHF, real UHF and complex UHF wavefunctions with direct energy minimization procedures to ensure finding stationary solutions. For real RHF (singlet states with $n_\alpha = n_\beta$) and real UHF (all n_α , n_β), programs for testing internal and external stability have been prepared, with additional provisions for further searches following detection of an instability. In this section, we describe some relevant features of these programs.

Given a stationary solution of the Hartree-Fock problem, stability is tested by constructing the appropriate matrix (Table I) and finding the complete set of eigenvalues. If one or more eigenvalues are strictly negative, instability is established and the corresponding eigenvectors \mathbf{D} give directions in which the energy will descend further. Zero eigenvalues may occur, but these do not imply instability.

Once an instability is found, a univariate energy search can be carried out in the appropriate direction to find a lower energy minimum. The technique used here is closely related to that developed previously for direct energy minimization to a stationary value.¹² Suppose χ^{SCF} are self-consistent spin orbitals corresponding to such a solution. Then, if ϵ is the diagonal

matrix of eigenvalues of the Fock operator at the (unstable) stationary point, and if D_s are elements of the eigenvector corresponding to a negative eigenvalue of the stability matrix (Table I), we may construct a generalized $(2N \times 2N)$ Fock matrix

$$\mathcal{F}(\lambda) = \epsilon + \lambda \begin{pmatrix} 0 & J^\dagger \\ J & 0 \end{pmatrix}, \quad (37)$$

where λ is a dimensionless path parameter and J is an $(2N-n) \times n$ matrix with elements

$$J_{at} = -(\epsilon_a - \epsilon_t)D_{t-a}. \quad (38)$$

The eigenvector matrix of $\mathcal{V}(\lambda)$ of this generalized Fock matrix will satisfy

$$\mathbf{V}^\dagger(\lambda)\mathcal{F}(\lambda)\mathbf{V}(\lambda) = \Gamma(\lambda), \quad (39)$$

where $\Gamma(\lambda)$ is diagonal. A new set of trial spin orbitals $\chi(\lambda)$ may then be obtained by transforming the self-consistent set χ^{SCF} according to

$$\chi(\lambda) = \chi^{\text{SCF}}\mathbf{V}(\lambda), \quad (40)$$

and this may be used to determine the energy $\mathcal{E}(\lambda)$ as a function of λ . Clearly $\lambda=0$ will lead to the unperturbed energy and

$$[d\mathcal{E}(\lambda)/d\lambda]_{\lambda=0} = 0, \quad (41)$$

since $\lambda=0$ corresponds to a stationary point. By analysis similar to that given in Ref. 12 it is easily shown that the initial change in the orbitals $\chi(\lambda)$ will be in the direction corresponding to the eigenvector D of this stability matrix. Also, the initial second derivative $[d^2\mathcal{E}(\lambda)/d\lambda^2]_{\lambda=0}$ will be equal to the corresponding (negative) eigenvalue.

The univariate search proceeds by taking finite steps in the parameter λ until a minimum of $\mathcal{E}(\lambda)$ is located at $\lambda = \lambda_{\text{min}}$. At each step, the selection of occupied spin orbitals is made by the criterion of overlap with the preceding set as described previously.¹² The new set of spin orbitals $\chi(\lambda_{\text{min}})$ will not usually be a solution of the Hartree-Fock equations, but may be used as a starting point for a further energy descent using the technique described in Ref. 12. In studies of internal instability, a search should be carried out in both di-

rections ($\lambda > 0$ and $\lambda < 0$) and both resulting minima should be used as starting points for subsequent energy minimization searches. For studies of external instabilities, on the other hand, the univariate search function $\mathcal{E}(\lambda)$ will be symmetric in λ . Hence only variation for $\lambda > 0$ is required.

V. CONCLUSION

The procedures outlined in earlier sections of this paper constitute a program for evaluating and testing Hartree-Fock wavefunctions at any level of constraint illustrated in Fig. 1. There are, of course, some limitations on what can be achieved. Although the direct energy descent features should ensure location of a stable solution at the constraint level desired, there is no guarantee that the resulting energy is the lowest achievable with single-determinant trial functions at this level. Also it is not yet clear whether some of the restrictions shown in Fig. 1 will ever lead to extension of the energy range achievable. Nevertheless, the procedures should provide a powerful tool for investigating conditions under which instabilities occur and for probing the limits of Hartree-Fock theory. Studies along these lines are under way.

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