

# Some Studies of the General Hartree-Fock Method

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## 1. History of the General Hartree-Fock Method

In the independent-particle-model (IPM) originally due to Bohr [1], each particle moves under the influence of the outer potential and the average potential of all the other particles in the system. In modern quantum theory, this model was first implemented by Hartree [2], who solved the corresponding one-electron Schrödinger equation by means of an iterative numerical procedure, which was continued until there was no change in the significant figures associated with the electric fields involved so that these could be considered as self-consistent; this approach was hence labelled the Self-Consistent-Field (SCF) method. In order to take the Pauli exclusion principle into account, Waller and Hartree [3] approximated the total wave function for a N-electron system as a product of two determinants associated with the electrons of

different spins. Somewhat later, Slater [4] introduced the spin coordinate  $\zeta$  and assumed that the one-electron functions involved  $\psi = \psi(\mathbf{x})$  depended on a combined space-spin coordinate  $\mathbf{x} = (\mathbf{r}, \zeta)$  and introduced further the convention that in calculating the binary product  $\langle \psi_1 | \psi_2 \rangle$  one should integrate over the space and sum over the spin. In treating a N-electron system in the independent-particle model, Slater approximated the total wave function  $\Psi$  by a *single determinant*  $\Psi \approx D$  formed by the one-electron functions  $\psi_1, \psi_2, \psi_3, \dots, \psi_N$ , which is antisymmetric and automatically satisfies the Pauli exclusion principle. In the Born-Oppenheimer approximation [5], the total Hamiltonian  $H$  for an atomic, molecular, or solid-state system containing  $N$  electrons has the form:

$$H = e^2 \sum_{g < h} Z_g Z_h / r_{gh} + \sum_i ( \mathbf{p}_i^2 / 2m - e^2 \sum_g Z_g / r_{ig} ) + \sum_{i < j} e^2 / r_{ij} \\ = H_{(0)} + \sum_i H_i + \sum_{i < j} H_{ij} , \quad (1.1)$$

Applying the variation principle  $\delta \langle H \rangle = 0$  to the total Hamiltonian  $H$  for the N-electron system, Slater [6] and Fock [7] derived effective one-electron equations of the form

$$F(1) \psi_k(\mathbf{x}_1) = \sum_l \psi_l(\mathbf{x}_1) \lambda_{lk}, \quad (1.2)$$

which became known as the Hartree-Fock (HF) equations. Slater had pointed out that - except for an irrelevant factor - the determinant  $D$  is invariant under a non-singular linear transformation of the one-electron functions  $\{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$ , which hence span a subspace of the total one-electron Hilbert space. The Lagrangian multipliers  $\lambda_{lk}$  form an hermitean matrix  $\lambda = \{\lambda_{lk}\}$ , and it could then be shown that the equations (1.2) by a unitary transformation could be brought to the simple form

$$F(1) \psi_k(\mathbf{x}_1) = \epsilon_k \psi_k(\mathbf{x}_1) , \quad (1.3)$$

where the eigenvalues  $\epsilon_k$  were interpreted as one-electron energies. There are different types of solutions for various types of Lagrangian multipliers  $\lambda = \{\lambda_{lk}\}$  - some are for instance localized - and it should be observed that the so-called *canonical Hartree-Fock functions* defined by (1.3) are always linear combinations of the other solutions. The effective Hamiltonian  $F(1)$  is often referred as the Fock-operator. Fock could show that, if the one-electron functions  $\psi = \{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$  are

chosen to be orthonormal, so that  $\langle \psi_k | \psi_l \rangle = \delta_{kl}$ , then the properties of the system is described by the density matrix

$$\rho(x_1, x_2) = \sum_k \psi_k(x_1) \psi_k^*(x_2) \quad (1.4)$$

where  $\rho(x_1, x_2)$  is the kernel of an operator  $\rho$  having the properties

$$\rho^2 = \rho, \quad \rho^\dagger = \rho, \quad \text{Tr } \rho = N. \quad (1.5)$$

The properties of the Hartree-Fock scheme were further investigated by Dirac [8], who showed that the Fock operator may be represented in the simple form

$$F(1) = H_1 + e^2 \int dx_2 \frac{\rho(2,2) - \rho(1,2) P_{12}}{r_{12}}, \quad (1.6)$$

where  $P_{12}$  is a permutation or exchange operator defined through the relation  $P_{12} u(1) = u(2)$ . The term containing  $P_{12}$  is often referred to as the *exchange term* in the Fock operator. It is then easily shown that the operator  $F$  has the property  $\langle v | Fu \rangle = \langle Fv | u \rangle$ , i.e. that the Fock operator is a self-adjoint one-electron operator. The kernel  $\rho(1,2)$  is often referred to as the Fock-Dirac density matrix, and it is evident that the operator  $\rho$  is the projector on the subspace spanned by the  $N$  one-electron functions. The one-electron energies  $\epsilon_k$  have finally been given a simple physical interpretation by Koopmans [9].

The one-electron functions  $\psi_k = \psi_k(x) = \psi_k(r, \zeta)$  are not restricted in any way - they are general *spin-orbitals* - and one may hence characterize this approach as the General Hartree-Fock (GHF) method. It should be observed, however, that the development of the Hartree-Fock scheme went in a different direction away from this general approach.. The calculations by Hartree in the years 1928-1933 [10] were carried out without exchange, and the first calculations *including exchange* were carried out on the ground state of the lithium atom by Fock and Petrashen [11]. The Li-atom in its ground state has the symmetry  $^2S$  and is characterized by the configuration  $(1s)^2(2s)$ , and it seemed hence natural to start the calculation from the configuration  $(1s\alpha, 1s\beta, 2s\alpha)$ , where  $\alpha$  and  $\beta$  are the elementary spin functions. These authors found - certainly somewhat to their surprise - that the calculations contained a *non-diagonal* Lagrangian multiplier  $\lambda_{1s,2s}$ , which could not be transformed

away as in the general theory. Constants of motion related to *symmetry properties* of the total Hamiltonian are, of course, of fundamental importance in quantum theory, and the question was now how they should be incorporated in the Hartree-Fock scheme. Already in 1930, it had been shown by Delbrück [12] that, if the total system has spherical symmetry and one assumes that the starting determinant has  $^1S$  symmetry, then this assumption is self-consistent, and the final Hartree-Fock functions turn out to be eigenfunctions of the orbital angular momentum and the spin. One could hence expect that the symmetry properties would be a natural part of any Hartree-Fock calculation.

In 1951, Slater [13] returned to this problem and pointed out that, if the Li-atom has the configuration  $(1s\alpha, 1s\beta, 2s\alpha)$ , then the  $1s\alpha$ -function is influenced by a different exchange potential than the  $1s\beta$ -function, since exchange occurs only between electrons with parallel spins, and one could then expect that the calculations would lead to two different  $1s$ -orbitals. Slater called this phenomenon *spin-polarization* or *spin-splitting*, and expected that it would be a small but important effect. Later applications at M.I.T. to open-shell systems [14] indicated that the effect was anything but small, and that it had many interesting consequences, particularly as to magnetic properties. A more detailed analysis of the new approach showed [15] that the spin-polarization was to some extent coupled with the *correlation splitting* due to the Coulomb repulsion, in which electrons with anti-parallel spins try to avoid each other by permitting "different orbitals for different spins" (DODS).

In the later part of the 1950's, it was evident that it was necessary to distinguish the new approach dealing with different orbitals for  $\alpha$ -spin and  $\beta$ -spin from the previous approach starting out from symmetry restrictions: the latter was called the Restricted Hartree-Fock (RHF) scheme, whereas the new approach was called the Unrestricted Hartree-Fock (UHF) scheme. For some time there was a certain amount of competition between the two schemes. In the late 1950's, it was further shown that the RHF-scheme for closed-shell systems was completely *self-consistent* not only for atoms but also for molecules and solids [16,17] and that, if one started by imposing a symmetry requirement on the original Slater determinant, this assumption would be self-consistent, i.e. the final determinant would have the same symmetry property. Since symmetry properties are of such fundamental importance in quantum theory, one would hence anticipate that the RHF-scheme would

be the fundamental one. The situation was complicated by the fact that, in many applications, the UHF-scheme would have a lower energy  $\langle H \rangle$  than the RHF-scheme.

In 1963, Löwdin [18] pointed out the occurrence of a *symmetry dilemma* in the Hartree-Fock method: that, even if a symmetry requirement is self-consistent, it is still a *constraint* which will increase the energy  $\langle H \rangle$ , and the associated optimum value of  $\langle H \rangle$  is hence only a *local minimum*; on the other hand, if one looks for the *absolute minimum* of  $\langle H \rangle$ , the associated Slater determinant may very well be a *mixture* of various symmetry types. It is evident that some of the optimum values of  $\langle H \rangle$  are not even local minima, and the study of the nature of the optimum values by means of the second-derivatives or the *Hessians* has become one of the most intensely studied problems [19] in the current literature. Most of the papers use very elegant and forceful methods based on the use of second quantization, but it should be observed that the problem may also be treated in an elementary way [20].

It should be observed that, even if the UHF-scheme is less restricted than the RHF-scheme, it still deals with pure  $\alpha$ - and  $\beta$ -functions, and it is hence restricted in comparison to the General Hartree-Fock (GHF) scheme, which deals with general one-electron functions of the form:

$$\psi_k(x) = \psi_k(r, \zeta) = \psi_{k+}(r) \alpha(\zeta) + \psi_{k-}(r) \beta(\zeta). \quad (1.7)$$

We note that the GHF-scheme is identical with the Hartree-Fock scheme originally derived by Fock and Slater, since in their derivations there were no restrictions imposed on the nature of the one-electron functions. This means that the GHF-scheme is still based on the equations (1.3)-(1.6). It should be observed that the functions  $\psi_{k+}(r)$  and  $\psi_{k-}(r)$  in general are of *complex* nature.

It is obvious that the Hartree-Fock equations are rather complicated integro-differential equations of a non-linear nature with bifurcations etc., and it was hence of fundamental importance when Lieb and Simon [21] in 1977 could show the *mathematical existence* of solutions to these equations. There are still some mathematical problems associated with the Hartree-Fock scheme, particularly the connection between the starting point of the calculations and the final result, which is usually associated with a "local minimum" of the energy  $\langle H \rangle$ . We note further that the concept of "self-consistency" is related to some form of "numerical convergence" in a specified number

of significant figures in the calculations and not to the concept of *mathematical convergence*, which is a problem that has so far not been sufficiently investigated. It should also be observed that the SCF-procedure is an iterative procedure which is subject to the laws discovered by Schröder [22] in 1870, which may be used to speed up the convergency or to change an obviously divergent process into a convergent one.

During the last decades, there has slowly been a return of the interest of the scientists working on many-fermion systems from the RHF- and UHF-schemes to the original Hartree-Fock scheme dealing with general spin-orbitals. In 1960, Overhauser [23] showed in a study of a one-dimensional Fermi gas that there existed self-consistent solutions in the form of giant "spin density waves" which had a lower energy than the plane-wave state, and in solid-state theory one has later shown the existence of both "spin-density waves" and "charge density waves", dealing with general spin-orbitals [24]. After the formulation of the "symmetry dilemma", some examples involving negative atomic ions were also given [25]. In nuclear physics as well as in the theory of electronic systems in general, the same problem was studied by Fukutome [26] who also developed a *general classification scheme* for the various general spin-orbitals occurring as solutions to the GHF-equations based on their symmetry properties, and introduced the terms time-reversal-invariant closed shell solutions (TICS), charge-current waves (CCW), axial spin waves (ASW), axial spin-current waves (ASCW), axial spin density waves (ASDW), torsional spin waves (TSW), torsional spin-current waves (TSCW), torsional spin density waves (TSDW), etc.

## 2. The General Hartree-Fock Equations; Separation of Space and Spin; the MO-LCAO-approach

Some notations. - Before starting the main part of this section, it may be convenient to discuss the use of some specific notations. Dirac [27] considered the bracket  $\langle x|y \rangle$  as the scalar product of a bra-vector  $\langle x|$  and a ket-vector  $|y \rangle$ , and - in this connection - he also introduced the ket-bra operators  $T = |b \rangle \langle a|$  defined through the relation  $Tx = b \langle a|x \rangle$ . They satisfy the relations  $T^2 = \langle a|b \rangle T$ ,  $T^\dagger = |a \rangle \langle b|$ , and  $\text{tr } T = \langle a|b \rangle$ .

In the following we will further use bold-face symbols **A** and **B** to denote rectangular matrices - including row and column vectors and quadratic matrices. If **A** and **B** are rectangular

matrices of order  $m \times p$  and  $p \times n$ , we will let the product  $\mathbf{C} = \mathbf{A} \mathbf{B}$  define a matrix of order  $m \times n$ , defined through the relation

$$(\mathbf{A} \mathbf{B})_{kl} = \sum_{\alpha} A_{k\alpha} B_{\alpha l}, \quad (2.1)$$

i.e. one multiplies the rows of the first matrix in order with the columns of the second matrix. As an illustration, we will consider the row vector formed by the one-electron functions  $\psi = \{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$ . The orthonormality property may now be expressed in the condensed form  $\langle \psi | \psi \rangle = 1$ , where as the Fock-Dirac operator may be written in the form  $\rho = |\psi \rangle \langle \psi|$ , i.e.

$$\rho = |\psi \rangle \langle \psi|, \quad \langle \psi | \psi \rangle = 1, \quad (2.2)$$

and the validity of the relations (1.5) becomes now clear and transparent in a somewhat new way.

If one instead starts from  $N$  one-electron functions  $\psi = \{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$ , which are linearly independent but not necessarily orthonormal, one may by means of symmetric orthonormalization [28] introduce an orthonormal set  $\phi = \psi \langle \psi | \psi \rangle^{-1/2}$ , which gives the projector

$$\rho = |\phi \rangle \langle \phi| = |\psi \rangle \langle \psi | \psi \rangle^{-1} \langle \psi|, \quad (2.3)$$

which has been studied in greater detail elsewhere [29].

The General Hartree-Fock equations. - The one-electron functions in the GHF-scheme are of the form (1.7) or

$$\psi_k(\mathbf{x}) = \psi_k(\mathbf{r}, \zeta) = u_k(\mathbf{r}) \alpha(\zeta) + v_k(\mathbf{r}) \beta(\zeta), \quad (2.4)$$

where the orbital functions  $u_k(\mathbf{r})$  and  $v_k(\mathbf{r})$  are in general complex functions. Introducing the row vectors  $\mathbf{u} = \{u_1, u_2, u_3, \dots, u_N\}$  and  $\mathbf{v} = \{v_1, v_2, v_3, \dots, v_N\}$ , one may write the relations (1.7) for  $k = 1, 2, 3, \dots, N$  in the condensed form

$$\psi = \mathbf{u} \alpha + \mathbf{v} \beta. \quad (2.5)$$

Since the spin functions  $\alpha$  and  $\beta$  are orthonormal, one gets directly

$$\langle \psi | \psi \rangle = \langle \mathbf{u} \alpha + \mathbf{v} \beta | \mathbf{u} \alpha + \mathbf{v} \beta \rangle = (\mathbf{u} | \mathbf{u}) + (\mathbf{v} | \mathbf{v}), \quad (2.6)$$

where the round brackets indicate binary products in the orbital space. In the following, we will use the notation

$$\mathbf{d} = \langle \psi | \psi \rangle^{-1}, \quad (2.7)$$

where  $\mathbf{d}$  is a matrix of order  $N \times N$  with the elements  $d_{kl}$ . According to (2.3), the Fock-Dirac operator takes now the form

$$\begin{aligned} \rho &= |\psi\rangle \langle \psi | \psi \rangle^{-1} \langle \psi | = |\psi\rangle \mathbf{d} \langle \psi | = \\ &= \sum_{k,l=1}^N |\psi_k\rangle d_{kl} \langle \psi_l|, \end{aligned} \quad (2.8)$$

where the double sum over  $k$  and  $l$  contains  $N^2$  terms, whereas for the associated density matrix one gets the formula

$$\rho(1,2) = |\psi(1)\rangle \mathbf{d} \langle \psi(2)| = \sum_{kl} \psi_k(1) d_{kl} \psi_l^*(2). \quad (2.9)$$

Substituting the expression (2.5) into (2.8), one gets further

$$\begin{aligned} \rho &= |\mathbf{u} \alpha + \mathbf{v} \beta\rangle \mathbf{d} \langle \mathbf{u} \alpha + \mathbf{v} \beta| = \\ &= \rho^{++} \alpha \alpha + \rho^{+-} \alpha \beta + \rho^{-+} \beta \alpha + \rho^{--} \beta \beta, \end{aligned} \quad (2.10)$$

where

$$\begin{aligned} \rho^{++} &= (\mathbf{u} | \mathbf{d} | \mathbf{u}), & \rho^{+-} &= (\mathbf{u} | \mathbf{d} | \mathbf{v}), \\ \rho^{-+} &= (\mathbf{v} | \mathbf{d} | \mathbf{u}), & \rho^{--} &= (\mathbf{v} | \mathbf{d} | \mathbf{v}). \end{aligned} \quad (2.11)$$

In this way, it is hence possible to separate the orbital parts and the spin parts of the Fock-Dirac operator in a simple way. The UHF-scheme, which deals with only pure  $\alpha$ - and  $\beta$ -functions, is characterized by the fact that one has  $\rho^{+-} = \rho^{-+} = 0$ , whereas in the GHF-scheme these components are always non-vanishing. According to (1.3), one may now write the Hartree-Fock equations in the form

$$F(1) \psi(1) = \psi(1) \varepsilon, \quad (2.12)$$

where  $\varepsilon$  is the diagonal matrix having the elements  $\varepsilon_k \delta_{kl}$ . According to (1.6), the Fock operator has here the form



$$\begin{aligned}
 F(1) &= H_1 + e^2 \int dx_2 \frac{\rho(2,2) - \rho(1,2) P_{12}}{r_{12}} = \\
 &= H_1 + J_1 - K_1, \quad (2.13)
 \end{aligned}$$

where  $J_1$  and  $K_1$  are the coulomb and exchange operators in the original Hartree-Fock scheme. This gives us directly

$$J_1 = e^2 \int dx_2 \frac{\rho(2,2)}{r_{12}} = e^2 \int dr_2 \frac{\rho^{++}(2,2) + \rho^{--}(2,2)}{r_{12}}, \quad (2.14)$$

where the quantity  $\{\rho^{++}(2,2) + \rho^{--}(2,2)\}$  in the numerator of the last integrand is the orbital density  $N(2,2)$  of electron 2. For the exchange operator, one gets in a similar way

$$K_1 = e^2 \int dx_2 \frac{\rho(1,2) P_{12}}{r_{12}}, \quad (2.15)$$

and further

$$\begin{aligned}
 K_1 \psi(1) &= e^2 \int dx_2 \frac{\rho(1,2) P_{12}}{r_{12}} \psi(1) = e^2 \int dx_2 \frac{\rho(1,2) \psi(2)}{r_{12}} = \\
 &= e^2 \int \frac{dx_2}{r_{12}} [\rho^{++}(1,2) \alpha_1 \alpha_2 + \rho^{+-}(1,2) \alpha_1 \beta_2 + \\
 &\quad \rho^{-+}(1,2) \beta_1 \alpha_2 + \rho^{--}(1,2) \beta_1 \beta_2] \times [\mathbf{u}(2) \alpha_2 + \mathbf{v}(2) \beta_2] = \quad (2.16) \\
 &= e^2 \int \frac{dx_2}{r_{12}} [\rho^{++}(1,2) \mathbf{u}(2) \alpha_1 + \rho^{+-}(1,2) \mathbf{v}(2) \alpha_1 + \\
 &\quad + \rho^{-+}(1,2) \mathbf{u}(2) \beta_1 + \rho^{--}(1,2) \mathbf{v}(2) \beta_1],
 \end{aligned}$$

where in the last line we have summed over the spin coordinate  $\zeta_2$ . At this point, it may be convenient to introduce the notation

$$K_1^{\mu\nu} = e^2 \int dr_2 \frac{\rho^{\mu\nu}(1,2) P_{12}^r}{r_{12}}, \quad (2.17)$$

where  $\mu, \nu = +, -$ , and the permutation operator  $P_{12}^r$  works only on the orbital coordinates. From the last line in equation (2.16), one hence obtains

$$\begin{aligned}
 K_1 \psi(1) &= K_1^{++} \mathbf{u}(1) \alpha_1 + K_1^{+-} \mathbf{v}(1) \alpha_1 + \\
 &\quad K_1^{-+} \mathbf{u}(1) \beta_1 + K_1^{--} \mathbf{v}(1) \beta_1. \quad (2.18)
 \end{aligned}$$

In studying the Hartree-Fock equations (2.12), one can now easily separate the  $\alpha$ - and  $\beta$ -components, and using (2.13) and (2.18), one obtains directly

$$(H_1 + J_1 - K_1^{++}) u(1) - K_1^{+-} v(1) = u(1) \varepsilon, \quad (2.19)$$

$$- K_1^{-+} u(1) + (H_1 + J_1 - K_1^{--}) v(1) = v(1) \varepsilon, \quad (2.20)$$

and it is then possible to combine these two relations into a matrix equation of the form

$$\begin{Bmatrix} H_1 + J_1 - K_1^{++} & -K_1^{+-} \\ -K_1^{-+} & H_1 + J_1 - K_1^{--} \end{Bmatrix} \begin{Bmatrix} u(1) \\ v(1) \end{Bmatrix} = \begin{Bmatrix} u(1) \\ v(1) \end{Bmatrix} \varepsilon. \quad (2.21)$$

We note that these equations for the  $2N$  orbital functions  $u$  and  $v$  are identical to the original Hartree-Fock equations and that no additional assumptions have been made.

### The MO-LCAO approach for solving the HF-equations. -

During the first 25 years of the development of the Hartree-Fock method, one used various types of numerical integration in connection with the SCF-procedures for studying atomic structures, and special methods were developed by Hartree [30]. There was also a renewed interest in the forceful central difference methods, which go back to Gauss [31]. However, in order to treat the electronic structure of *molecules* by the Hartree-Fock method, there were evidently some new ideas needed. Already in 1928, it had been shown by Mulliken and Hund [32] that one can obtain a good understanding of molecular structure by means of the concept of *molecular orbitals*, and very often these molecular orbitals (MO's) could be constructed by means of linear combination of atomic orbitals (LCAO) [33]. This idea forms the basis for the MO-LCAO approach, and it was first shown by Roothaan in the late 1940's and early 50's how this method can be formulated in a self-consistent-field way [34]. In this connection, a great deal of work had to be devoted to the problem of calculating one-, two-, three-, and four-center *molecular integrals* involving atomic orbitals, e.g. Slater-type orbitals (STO's). With the development of the modern electronic computers, this problem could be partly circumvented by following Boys' [35] suggestion of using a network of Gaussian orbitals.

Let us assume that  $\bar{\Phi} = \{\bar{\Phi}_1, \bar{\Phi}_2, \bar{\Phi}_3, \dots, \bar{\Phi}_{M'}\}$  is a set of linearly independent one-electron functions with  $M' \geq N$ , having a metric matrix  $\bar{\Delta} = \langle \bar{\Phi} | \bar{\Phi} \rangle$  and that the Hartree-Fock functions  $\psi = \{\psi_1, \psi_2, \psi_3, \dots, \psi_N\}$  are formed by linear combinations of these basis functions, so that  $\psi = \bar{\Phi} \mathbf{c}$ , where  $\mathbf{c}$  is a rectangular coefficient matrix of order  $M' \times N$ . If the set  $\psi$  is orthonormal, one gets directly the condition  $\langle \psi | \psi \rangle = \langle \bar{\Phi} \mathbf{c} | \bar{\Phi} \mathbf{c} \rangle = \mathbf{c}^\dagger \bar{\Delta} \mathbf{c} = 1$ . In such a case, the Fock-Dirac operator takes the form  $\rho = |\psi\rangle\langle\psi| = |\bar{\Phi} \mathbf{c}\rangle\langle\bar{\Phi} \mathbf{c}| = |\bar{\Phi}\rangle \mathbf{c} \mathbf{c}^\dagger \langle\bar{\Phi}| = |\bar{\Phi}\rangle \mathbf{R} \langle\bar{\Phi}|$ , where  $\mathbf{R} = \mathbf{c} \mathbf{c}^\dagger$  is closely associated with the so-called charge- and bond-order matrix originally introduced by Coulson and Longuet-Higgins [36]. Since the matrix  $\mathbf{R}$  of order  $M' \times M'$  has the properties  $\mathbf{R} \bar{\Delta} \mathbf{R} = \mathbf{R}$ ,  $\mathbf{R}^\dagger = \mathbf{R}$ ,  $\text{tr}(\mathbf{R} \bar{\Delta}) = N$ , it reflects the properties of the projector  $\rho$  as expressed in (1.5). The more detailed properties of the matrix  $\mathbf{R}$  and its importance for the SCF-procedure have been studied elsewhere [37].

Let us now study exactly the same approach when we like to separate the space and spin functions, and let us assume that  $\Phi = \{\Phi_1, \Phi_2, \Phi_3, \dots, \Phi_M\}$  is a linearly independent *orbital basis* of order  $M$  with the metric matrix  $\Delta = \langle \Phi | \Phi \rangle$ . In such a case, one can construct a spin-orbital basis of the form  $\bar{\Phi} = \{\Phi_\alpha, \Phi_\beta\}$  having  $M' = 2M$  and the metric matrix

$$\bar{\Delta} = \begin{Bmatrix} \Delta & \mathbf{0} \\ \mathbf{0} & \Delta \end{Bmatrix}. \quad (2.22)$$

Let us express the orbital functions  $\mathbf{u}$  and  $\mathbf{v}$  in (2.5) in terms of the orbital basis  $\Phi$  in the form:

$$\mathbf{u} = \Phi \mathbf{a}, \quad \mathbf{v} = \Phi \mathbf{b}, \quad (2.23)$$

where  $\mathbf{a}$  and  $\mathbf{b}$  are row vectors of order  $M$ . For the sake of simplicity, we will choose the orbital basis  $\Phi$  *real*, whereas the coefficient vectors  $\mathbf{a}$  and  $\mathbf{b}$  may be *complex*. Hence we have

$$\psi = \mathbf{u} \alpha + \mathbf{v} \beta = \Phi \mathbf{a} \alpha + \Phi \mathbf{b} \beta = \bar{\Phi} \mathbf{c}, \quad (2.24)$$

where

$$\mathbf{c} = \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \end{pmatrix} \quad (2.25)$$

is a column vector of order  $M' = 2M$ , and further

$$\begin{aligned} \langle \psi | \psi \rangle &= \langle \Phi \mathbf{a} \alpha + \Phi \mathbf{b} \beta | \Phi \mathbf{a} \alpha + \Phi \mathbf{b} \beta \rangle = \\ &\quad \mathbf{a}^\dagger \langle \Phi | \Phi \rangle \mathbf{a} + \mathbf{b}^\dagger \langle \Phi | \Phi \rangle \mathbf{b} = \\ &\quad = \mathbf{a}^\dagger \Delta \mathbf{a} + \mathbf{b}^\dagger \Delta \mathbf{b} = \mathbf{c}^\dagger \bar{\Delta} \mathbf{c}, \end{aligned} \quad (2.26)$$

Recalling the notation  $\mathbf{d} = \langle \psi | \psi \rangle^{-1}$ , one obtains according to (2.8) for the Fock-Dirac operator

$$\begin{aligned} \rho &= |\psi \rangle \langle \psi | \psi \rangle^{-1} \langle \psi | = |\psi \rangle \mathbf{d} \langle \psi | = \\ &\quad |\Phi \mathbf{a} \alpha + \Phi \mathbf{b} \beta \rangle \mathbf{d} \langle \Phi \mathbf{a} \alpha + \Phi \mathbf{b} \beta | = \\ &\quad = \rho^{++} \alpha \alpha + \rho^{+-} \alpha \beta + \rho^{-+} \beta \alpha + \rho^{--} \beta \beta, \end{aligned} \quad (2.27)$$

where

$$\begin{aligned} \rho^{++} &= |\Phi \rangle \mathbf{a} \mathbf{d} \mathbf{a}^\dagger \langle \Phi | = |\Phi \rangle \mathbf{R}^{aa} \langle \Phi |, \\ \rho^{+-} &= |\Phi \rangle \mathbf{a} \mathbf{d} \mathbf{b}^\dagger \langle \Phi | = |\Phi \rangle \mathbf{R}^{ab} \langle \Phi |, \\ \rho^{-+} &= |\Phi \rangle \mathbf{b} \mathbf{d} \mathbf{a}^\dagger \langle \Phi | = |\Phi \rangle \mathbf{R}^{ba} \langle \Phi |, \\ \rho^{--} &= |\Phi \rangle \mathbf{b} \mathbf{d} \mathbf{b}^\dagger \langle \Phi | = |\Phi \rangle \mathbf{R}^{bb} \langle \Phi | \end{aligned} \quad (2.28)$$

Here the quantities

$$\mathbf{R}^{aa} = \mathbf{a} \mathbf{d} \mathbf{a}^\dagger, \mathbf{R}^{ab} = \mathbf{a} \mathbf{d} \mathbf{b}^\dagger, \mathbf{R}^{ba} = \mathbf{b} \mathbf{d} \mathbf{a}^\dagger, \mathbf{R}^{bb} = \mathbf{b} \mathbf{d} \mathbf{b}^\dagger, \quad (2.29)$$

are matrices of order  $M \times M$ , which may be combined into a single matrix  $\mathbf{R} = \mathbf{c} \mathbf{d} \mathbf{c}^\dagger$  of order  $2M \times 2M$  in agreement with the general theory. In the case when the Hartree-Fock functions  $\psi$  are orthonormal, one has of course  $\mathbf{d} = \mathbf{1}$ .

One can now substitute the expressions for  $\mathbf{u}$  and  $\mathbf{v}$  into the equations (2.21) provided that one observes that these equations are *exact* in the original Hartree-Fock scheme, whereas we are here using a truncated orbital basis of order  $M$ . Multiplying these relations to the left by  $\langle \Phi(1) |$  and integrating over  $\mathbf{r}_1$ , one obtains instead the matrix equations

$$\begin{Bmatrix} \mathbf{h} + \mathbf{J} - \mathbf{K}^{++}; & -\mathbf{K}^{+-} \\ -\mathbf{K}^{-+}; & \mathbf{h} + \mathbf{J} - \mathbf{K}^{--} \end{Bmatrix} \begin{Bmatrix} \mathbf{a} \\ \mathbf{b} \end{Bmatrix} = \begin{Bmatrix} \Delta & \mathbf{0} \\ \mathbf{0} & \Delta \end{Bmatrix} \begin{Bmatrix} \mathbf{a} \\ \mathbf{b} \end{Bmatrix} \varepsilon. \quad (2.30)$$

In the standard way, it may be proven by means of the variation principle applied to the Fock-operator  $F(1)$  that these equations give the best approximations to the Hartree-Fock functions in the truncated orbital basis of order  $M$ . For the matrices involved, one gets the following expressions

$$\mathbf{h} = \langle \Phi(1) | H_1 | \Phi(1) \rangle = \langle \Phi(1) | \mathbf{p}_1^2/2m - \sum_g e^2/r_{1g} | \Phi(1) \rangle, \quad (2.31)$$

$$\begin{aligned} \mathbf{J} &= \langle \Phi(1) | J_1 | \Phi(1) \rangle = \\ &= e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \Phi(1) \frac{\rho^{++}(2,2) + \rho^{--}(2,2)}{r_{12}} \Phi(1), \end{aligned} \quad (2.32)$$

$$\mathbf{K}^{\mu\nu} = \langle \Phi(1) | K_1^{\mu\nu} | \Phi(1) \rangle = e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \Phi(1) \frac{\rho^{\mu\nu}(1,2)}{r_{12}} \Phi(2), \quad (2.33)$$

where in the last line  $\mu, \nu = +, -$ . For the quantities  $\rho^{\mu\nu}(1,2)$ , one has further according to (2.28) and (2.29):

$$\rho^{\mu\nu}(1,2) = \Phi(1) R^{\mu\nu} \Phi(2) = \sum_{\kappa\lambda} \Phi_{\kappa}(1) R^{\mu\nu}_{\kappa\lambda} \Phi_{\lambda}(2), \quad (2.34)$$

where on the right-hand sides one has now  $\mu, \nu = a, b$ . In the theory of molecular integrals, one is using the two notations

$$\begin{aligned} (\mu\kappa | \frac{e^2}{r_{12}} | \lambda\nu) &= e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Phi_{\mu}(1)\Phi_{\kappa}(2)\Phi_{\lambda}(1)\Phi_{\nu}(2)}{r_{12}} = \\ &= (\mu\lambda | \kappa\nu), \end{aligned} \quad (2.35)$$

where the last one is the well-known "Mulliken notation", which refers to the two charge densities involved and has some obvious symmetry properties. For the matrix elements of the three fundamental matrices, one hence obtains

$$\begin{aligned} h_{kl} &= \langle \Phi_k(1) | H_1 | \Phi_l(1) \rangle = \\ &= \langle \Phi_k(1) | \mathbf{p}_1^2/2m - \sum_g e^2/r_{1g} | \Phi_l(1) \rangle, \end{aligned} \quad (2.36)$$

$$\begin{aligned} J_{kl} &= \langle \Phi_k(1) | J_1 | \Phi_l(1) \rangle = \\ &= e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \Phi_k(1) \frac{\rho^{++}(2,2) + \rho^{--}(2,2)}{r_{12}} \Phi_l(1) = \end{aligned}$$

$$\begin{aligned}
&= \sum_{\kappa\lambda} (R^{aa}_{\kappa\lambda} + R^{bb}_{\kappa\lambda}) e^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Phi_{\kappa}(1)\Phi_{\kappa}(2)\Phi_{\lambda}(2)\Phi_{\lambda}(1)}{r_{12}} = \\
&= \sum_{\kappa\lambda} (R^{aa}_{\kappa\lambda} + R^{bb}_{\kappa\lambda}) (\kappa\lambda | \kappa\lambda), \quad (2.37)
\end{aligned}$$

$$\begin{aligned}
K^{\mu\nu}_{\mathbf{kl}} &= \langle \Phi_{\mathbf{k}}(1) | K_1^{\mu\nu} | \Phi_{\mathbf{l}}(1) \rangle = \\
&= e^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{\mathbf{k}}(1) \frac{\rho^{\mu\nu}(1,2)}{r_{12}} \Phi_{\mathbf{l}}(2) = \\
&= \sum_{\kappa\lambda} (R^{\mu\nu}_{\kappa\lambda} + R^{\mu\nu}_{\kappa\lambda}) e^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Phi_{\kappa}(1)\Phi_{\kappa}(1)\Phi_{\lambda}(2)\Phi_{\lambda}(2)}{r_{12}} = \\
&= \sum_{\kappa\lambda} (R^{\mu\nu}_{\kappa\lambda} + R^{\mu\nu}_{\kappa\lambda}) (\kappa\kappa | \lambda\lambda), \quad (2.38)
\end{aligned}$$

where in the last relation one has  $\mu, \nu = +, -$  or  $a, b$ , respectively. We note that, within the orbital subspace of order  $M$ , the equations (2.30) are identical with the original Hartree-Fock equations without any additional assumptions. We note further that, whereas the orbital basis  $\Phi$  was assumed to be *real*, the vectors  $\mathbf{a}$  and  $\mathbf{b}$  may have *complex* character. From the point of view of interpretations, it is sometimes preferable to introduce - instead of the four components  $\rho^{++}$ ,  $\rho^{+-}$ ,  $\rho^{-+}$ , and  $\rho^{--}$  - the *number density matrix*  $N(1,2)$  and the *spin density vector*  $\mathbf{S}(1,2) = \{S_1, S_2, S_3\}$  defined through the relations

$$N(\mathbf{r}_1, \mathbf{r}_2) = \int \rho(\mathbf{r}_1, \zeta; \mathbf{r}_2, \zeta) d\zeta = \rho^{++}(\mathbf{r}_1, \mathbf{r}_2) + \rho^{--}(\mathbf{r}_1, \mathbf{r}_2), \quad (2.39)$$

$$\mathbf{S}(\mathbf{r}_1, \mathbf{r}_2) = \int \mathbf{s} \rho(\mathbf{r}_1, \zeta; \mathbf{r}_2, \zeta) d\zeta, \quad (2.40)$$

where the latter quantity has the three components:

$$\begin{aligned}
S_1(1,2) &= [\rho^{+-}(1,2) + \rho^{-+}(1,2)]/2, \\
S_2(1,2) &= [\rho^{+-}(1,2) - \rho^{-+}(1,2)]/2, \\
S_3(1,2) &= [\rho^{++}(1,2) - \rho^{--}(1,2)]/2,
\end{aligned} \quad (2.41)$$

see e.g. the first reference in [20] or [24].

The problem associated with the solution of the matrix equations (2.30) is to explore the energy surface  $\langle H \rangle$  for the total Hamiltonian  $H$ , to study its local minima and extreme values, and - if possible - to find the absolute energy minimum connected with the Hartree-Fock method. Thanks to Fukutome's work [26], this problem has now been essentially

simplified, since one knows that every solution to the general Hartree-Fock equations corresponding to an energy minimum of  $\langle H \rangle$  must belong to one of Fukutome's eight classes. The most restricted one is, of course, the RHF-solution, whereas the most general one is the one called "Torsional Spin Waves" (TSW).

Some Applications. - Looking at the literature, one finds that, in atomic and molecular physics, comparatively little interest has so far been devoted to the GHF-scheme, and the purpose of this paper is to try to focus the interests of some quantum chemists to this rather interesting problem of looking for the "absolute minimum" of the original Hartree-Fock method.

Since the general spin-orbitals (GSO's) of type (2.4) contain twice as many orbital functions as the one-electron functions used in the UHF-scheme, one could perhaps expect that, even for atomic and molecular systems, the GHF-method would give a lower variational energy than the UHF-method [38]. Applications to some two-electron systems - the helium-like ions and the hydrogen molecule - by Lunell [39] showed, however, that the GHF-scheme converged to exactly the same energy as the UHF-scheme. Physically this depends probably on the fact that a two-electron system has its lowest energy when the two electrons have opposite spins. As an introduction, we repeated these calculations by means of somewhat different computational tools - with starting points also in the complex plane - with the same result, but we still have not been able to give a simple mathematical proof that, for two-electron systems, the GHF- and the UHF-methods give the same result. This is hence still an open question.

Even if some interesting applications of the GHF-method had been found in solid-state theory [23,24], the applications to molecular systems were comparatively few [40]. One major application to molecular systems had been worked out by Fukutome [40], and it was a study of the properties of the polyacetylene by means of the Pariser-Parr-Pople (PPP) approximation. It seemed hence desirable to make a molecular study based on *ab-initio* calculations to verify that one would get similar results and to get some experience in handling general Hartree-Fock orbitals of a complex nature, and for this purpose we started with some simple applications to atoms and to the BH molecule.

### 3. Applications of the General Hartree-Fock Theory to some Atoms and the BH Molecule

The programming of the GHF equations (2.21) in matrix form (2.30) was carried out in a straightforward manner: the one- and two-electron integrals were calculated by a slightly modified version of the well-known GAUSSIAN-70 package [41]. The SCF calculations were carried out by using rather strict convergence criteria: a numerical convergence of about  $10^{-10}$  a.u. in the energy and  $10^{-7}$  to  $10^{-8}$  in each element of the matrix  $\mathbf{R}$  have been required as the largest permitted changes in an SCF cycle. The achievement of this degree of convergence often required a very large number of iteration steps in the SCF procedure (sometimes several hundred or even one or two thousand), because the energy hypersurfaces as functions of the orbital coefficients turned out to be extremely flat. (This behaviour was partly due to the existence of some orientational arbitrariness in the problems studied, which will be discussed later, and in some cases due also to the occurrence of different solutions in very near vicinity of each other). No extrapolation methods were applied to speed up the convergence in order to avoid "jumps" from one branch of solutions to the other. Since we used a basis consisting of real Gaussians, we have carefully considered the case of complex LCAO coefficients, and it is hence remarkable that all the wave functions actually obtained in the calculations were expressible by means of real coefficients.

Some crucial aspects of studying the GHF wave functions are connected with the relationship between the GHF and UHF methods. First of all, it is evident that the RHF and UHF wave functions are particular solutions also to the GHF problem: In this case the components  $\rho^{+-}$  and  $\rho^{-+}$  of the Fock-Dirac density matrix are zero, and the GHF equations separate into two sets of equations for the orbitals of spins  $\alpha$  and  $\beta$ , respectively. The system of equations obtained in this way is identical to that of the ordinary UHF scheme. We note that the two sets of equations are still coupled through the components  $\rho^{++}$  and  $\rho^{--}$ . The situation is in some way analogous to the case of the UHF equations for a closed-shell system, for which the RHF functions always provide a particular solution. Similarly to the RHF versus UHF case, the UHF (or RHF) solution can, in principle, represent either a true (local) minimum or a saddle point for the GHF problem.

There is another aspect which makes it somewhat difficult to find genuine GHF solutions. Since the conventional RHF and



UHF schemes are characterized by vanishing components  $\rho^{+-}$  and  $\rho^{-+}$ , it is obviously a *necessary* condition for the existence of the GHF solution that these components are non-vanishing:  $\rho^{+-} = (\rho^{-+})^\dagger \neq 0$ . At the same time, it should be observed that this condition is far from *sufficient*, since the energy is independent of the axes of the spin quantization [39]. The basic Hamiltonian (1.1) does not contain the spin, and it is invariant under rotations of the underlying three-dimensional Euclidean space. When the coordinate space (x,y,z) is rotated, the spin functions undergo a unitary transformation:

$$\alpha' = \alpha u_{11} + \beta u_{21}, \quad \beta' = \alpha u_{12} + \beta u_{22}, \quad (3.1)$$

where the coefficients form a two-dimensional unitary matrix  $u = \{u_{ki}\}$ . If one replaces the spin functions  $\alpha$  and  $\beta$  in a set of  $N$  conventional UHF function  $\psi$  with  $\alpha'$  and  $\beta'$ , one obtains a set of new UHF function  $\psi'$  which look like GHF functions (1.7) and which have a Fock-Dirac density matrix with  $\rho^{+-} = (\rho^{-+})^\dagger \neq 0$ , but which still have the same orbital energies and total energy. If one starts from the assumption that a *genuine GHF solution*, due to the richer possibilities for variation, should have a lower energy than the UHF solution, then one has to exclude the spin rotated UHF functions. In our calculations, we hence checked this possibility by investigating whether the matrix  $R^{ab}$  defined by (2.29) could be reduced to zero by a spin rotation of type (3.1). For a genuine GHF solution, such a reduction should, of course, not be possible.

The simplest system we considered was the  $H_2$  molecule treated at the STO-6G and 4-31G levels; for this molecule, however, we could not obtain any GHF solution with an energy lower than the UHF one. In the minimum basis case, we have also explored the energy hypersurface in somewhat greater detail by introducing a dense mesh of the independent parameters defining the two-electron wave function and calculating its energy in all points of the mesh; even in this way no GHF energy lower than the UHF energy could be found. This result seems to indicate that in this case there is no genuine GHF solution, and that it is identical to the UHF solution. As we mentioned at the end of the previous section, this result for a two-electron system depends probably *physically* on the fact that the total energy is lowest when the spins  $\alpha$  and  $\beta$  - or more generally  $\alpha'$  and  $\beta'$  - have opposite spin directions. It remains to prove this statement also mathematically.

In studying atoms, no genuine GHF solutions could be obtained for the case of the He and Li atoms, either, in accordance with some previous results [39].

The simplest system for which a specific GHF solution has been obtained is the Be atom treated at the STO-6G level. Table 1 summarizes the energy values obtained for the  $(1s)^2(2s)^2$  ground state of this atom by the RHF, UHF, and GHF, as well as those obtained for the triplet and singlet excited states. (The triplet state corresponded to  $S_z = 1$  and was calculated by the UHF scheme, while the excited singlet describes an RHF configuration). For the UHF wave function a simultaneous breaking of both spatial and spin symmetries takes place, and the UHF energy is significantly lower than the RHF one. This UHF energy lowering ( $1.7 \times 10^{-3}$  a.u.) can most likely be related to the existence of a low-lying triplet state and to the "quasi-degeneracy" between between the 2s and 2p orbitals reducing the value of the first singlet-singlet excitation energy. The GHF method gives an additional energy lowering of  $1.2 \times 10^{-4}$  a.u.; this relationship between the energy gains in the UHF and GHF methods can be considered rather typical also for the other cases we have considered.

Both the UHF and the GHF methods give a partial description of the angular correlation in the Be atom: there is a small admixture of the 2p basis orbitals in the SCF orbitals describing the 2s shell (and, to a less extent, the 1s shell). For beryllium treated in a minimal basis set, there is no possibility to describe any radial correlation. The GHF wave functions obtained for models with split valence shell (6-31G or 4-31G) basis sets, which we will discuss below, give a partial account of both radial (or left-right) and angular correlation. However, the effect of the latter seems to be crucial for the very existence of the genuine GHF solutions, similar to the specific (both spin- and symmetry-unrestricted) UHF solutions to which they are close. A comparison with Fukutome's scheme shows that these GHF functions are Torsional Spin Density Waves (TSDW).

The typical GHF picture may perhaps best be seen by considering the expansion of the pair of GHF 2s orbitals of the Be atom:

$$\begin{aligned}\psi_3 = & -0.270\phi(1s).\alpha + 0.996\phi(2s).\alpha \\ & + 0.189\phi(2p_y).\alpha + 0.189\phi(2p_x).\beta, \\ \psi_4 = & -0.270\phi(1s).\beta + 0.996\phi(2s).\beta \\ & - 0.189\phi(2p_y).\beta + 0.189\phi(2p_x).\alpha,\end{aligned}\tag{3.2}$$

These equations indicate that both 2s orbitals have admixtures of two different p-orbitals, one with  $\alpha$  spin and one with  $\beta$  spin, with equal absolute values of the coefficients but with a characteristic difference in the phases for the two orbitals. The equal absolute values of the coefficients imply that such pairs of GHF orbitals of TSDW type have identical orbital energies.

The next system under consideration was the carbon atom. Table 2 shows the energies obtained for the carbon atom by using 4-31G and 6-31G basis sets. The overall behaviour of the solutions is similar to that in the beryllium case. For carbon, however, the true ground state is a triplet in accordance with Hund's rule. The GHF energy obtained is significantly lower than the singlet RHF one, but it is higher than the triplet UHF value. This means that the GHF wave function obtained represents a mixture of singlet and triplet states, which leads to a stationary value of the energy but not to its absolute minimum. In such a case, it is probably not meaningful to discuss to what extent electron correlation is accounted for by the GHF method. It does not seem to be excluded that another GHF solution with an energy lower than the triplet UHF may exist, but we made no special search for such a solution, since we wanted to go on to the molecular case.

Several calculations for the BH molecule at the 4-31G level were also performed. This molecule is a very interesting species: it is a closed-shell  $\sigma$ -system which is, at the same time, paramagnetic. In the RHF or conventional (spin-unrestricted) UHF approaches, all the  $\sigma$ -orbitals are empty; its characteristic magnetic behaviour may then tentatively be connected with the low excitation energies needed to transfer an electron to the low-lying excited  $\sigma$ -levels.

For the BH molecule *six different solutions* of the GHF equations were obtained: one RHF solution, three different UHF solutions, and two different genuine GHF solutions of TSDW type. A part of these solutions exists only at some values of the intermolecular distance; there is, however, a narrow interval for which all six solutions were obtained simultaneously.

Fig. 1a shows an overall view of the potential curves of the BH molecule corresponding to the different SCF solutions. The RHF solution exists, in principle, at all intermolecular distances  $R$ , although - for  $R > 3.5 \text{ \AA}$  - the conventional SCF procedure does not converge. (This is quite typical for similar systems). At large distances, the RHF curve shows the well-known incorrect

Table 1.

Energies of the Be atom  
calculated by using a STO-6G  
basis set.

Wave function	Energy in a.u.
RHF	-14.503 361
UHF( $S_z=0$ )	-14.505 074
GHF	-14.505 190
Triplet (UHF, $S_z=1$ )	-14.442 082
Singlet ( $1s$ ) <sup>2</sup> ( $2p$ ) <sup>2</sup>	-14.172 547

Table 2.

Energies of the carbon atom  
calculated by using 4-31G and  
6-31G basis sets.

Wave function	Energies in a.u.	
	4-31G	6-31G
RHF	-37.544 557	-37.588 204
UHF ( $S_z=0$ )	-37.604 05	-37.647 030
GHF	-37.612 63	-37.655 524
Triplet (UHF, $S_z=1$ )	-37.635 05	-37.677 837

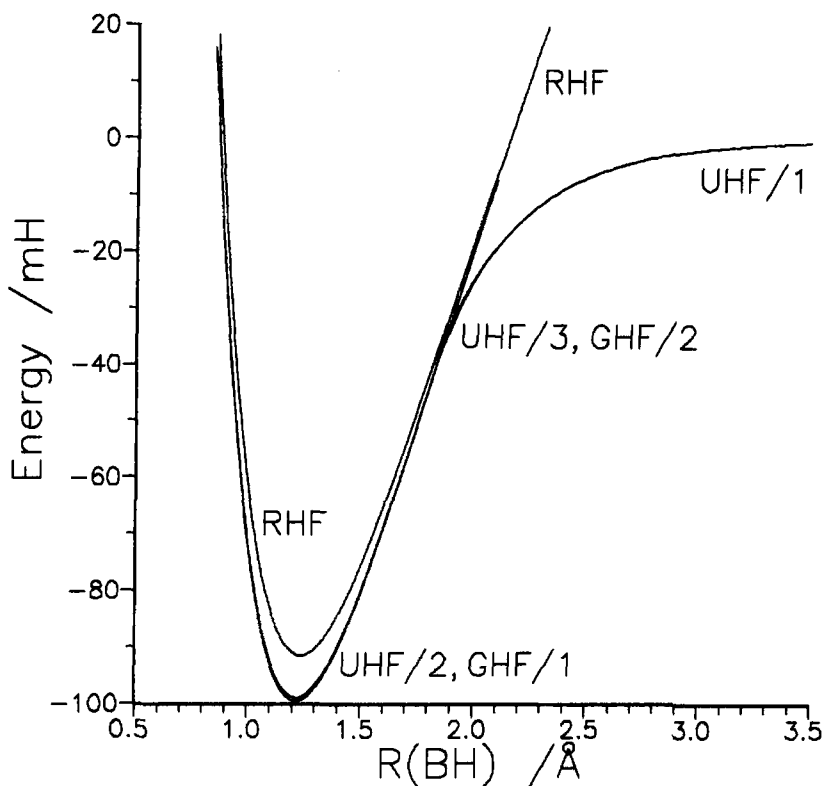


Figure 1a

dissociation behaviour [42] connected with the large weight of the ionic configurations in the RHF wave functions built up of doubly filled orbitals. This wrong asymptotic behaviour is corrected by the usual UHF wave function (denoted here as UHF/1). At  $R \sim 1.8 \text{ \AA}$ , the UHF/1 potential curve smoothly departs from the RHF one and tends to a correct limiting value at  $R \rightarrow \infty$ , giving a basically adequate description of the main features of the left-right correlation. However, as discussed in [43], the UHF potential curve makes a short turn after departing from the RHF one and approaches the (correct) limiting value too quickly. This is connected with the sudden appearance of the specific UHF solution differing from the RHF one, and indicates that the UHF wave functions do not have enough flexibility to describe properly the binding effects and to reduce effectively the weight of the ionic terms. Therefore, there is a too quick transition between the limiting cases for which essentially one of these factors is taken into account. (The RHF method is better for describing the binding effects, and the usual UHF solution appears only when they are overweighted by the left-right correlation.) As discussed in [43], this defect cannot be eliminated by using single determinant wave functions, while it does not occur in the projected (extended) Hartree-Fock method. (In the present case, besides the usual RHF and UHF wave functions, there are several other single determinant SCF wave functions of the UHF and GHF type. Neither of them solves, however, this problem of the too fast transition between the bonding and asymptotic regions.) In the bifurcation point, the UHF/1 potential curve merges continuously with the RHF one and has also a first derivative, coinciding with that of the RHF wave functions, but there is a discontinuity in its second derivative [43].

Analogously to all similar UHF wave functions describing dissociation of a closed shell molecule into two odd-electron fragments, the UHF/1 wave functions is characterized by a pair of molecular orbitals of opposite spins, which are more and more localized on the boron and on the hydrogen, respectively, as the internuclear distance  $R$  increases. (In the limit  $R \rightarrow \infty$ , one of these orbitals becomes a pure boron, another a pure hydrogen atomic orbital).

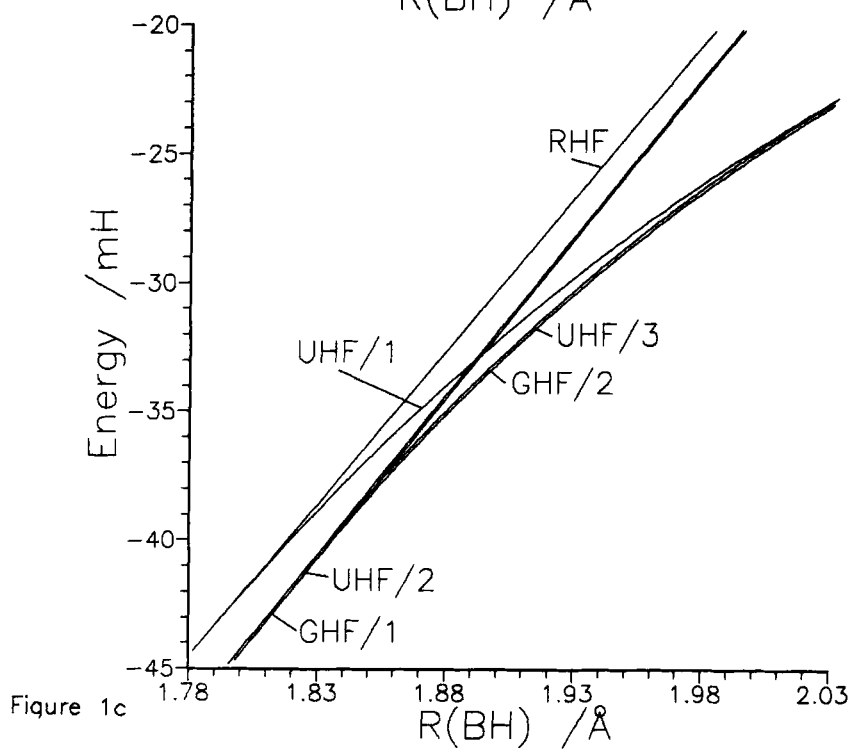
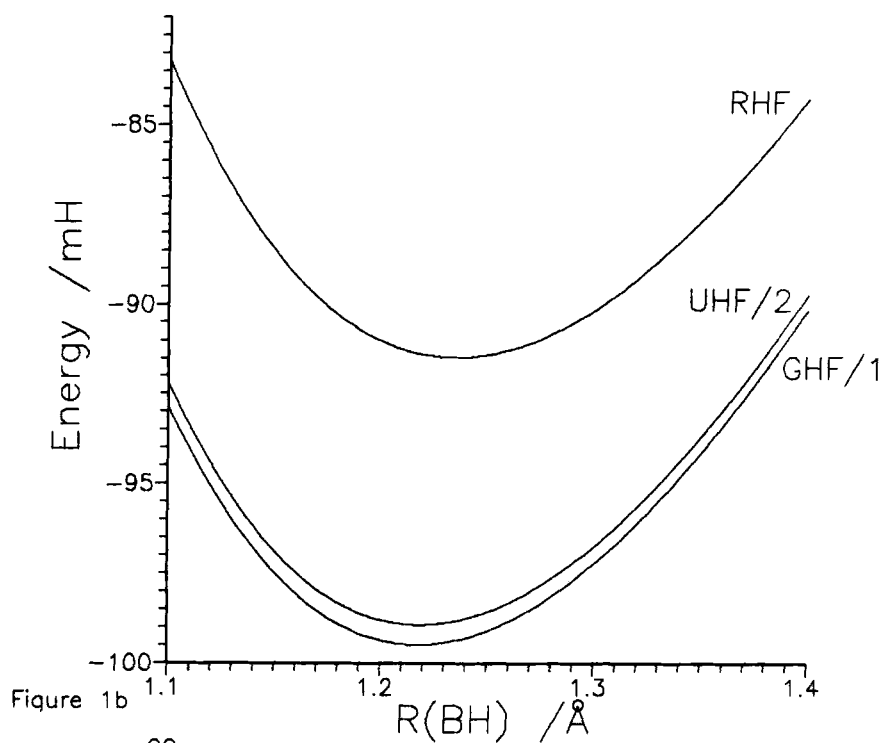
At the equilibrium internuclear distance, there are two solutions with energies lower than the RHF one (Fig. 1b). The curve denoted UHF/2 corresponds to a spin- and spatially-unrestricted single determinant wave function, in which the  $\sigma$ -orbitals contain some admixture of the  $\pi$ -type 2p boron orbitals, which are empty in both the RHF and UHF/1 wave functions.

The GHF/1 solution differs from the UHF/2 one by a small admixture of  $\pi$ -orbitals of opposite spin. This is a genuine GHF solution which cannot be reduced to a UHF one by any rotation of the spin axes.

All the three solutions existing in the interval around the equilibrium internuclear distance give the position of the minimum on the potential curve at about 1.22 - 1.23 Å, which is in good agreement with the experimental value 1.232 Å [44]. Neither of the UHF/2 or GHF/1 wave functions describe any left-right correlation: in both cases there are three pairs of molecular orbitals characterized by degenerate orbital energies and strictly equal coefficients of the boron  $\sigma$ -orbitals as well of the hydrogen AO's. These orbitals differ only in the admixtures of the  $\pi$ -orbitals, in a manner analogous to the beryllium example described in (3.2). Accordingly the UHF/2 and GHF/1 potential curves exhibit a wrong dissociation behaviour, quite analogous to that of the RHF curve.

Due obviously to the increasing importance of the left-right correlation, the UHF/2 and GHF/1 solutions become *numerically* unstable at larger internuclear distances. At the distance  $R = 2.05$  Å, the SCF procedure started from the orbitals obtained at  $R = 2.00$  Å give first convergence to a UHF/2 or GHF/1 wave function, respectively. (Convergence up to  $\sim 10^{-5}$  in the R-matrix elements and  $\sim 10^{-8}$  a.u. in the energy has been obtained). Then - under the influence of the rounding-off errors - the calculation departed slowly from the domain of the wave functions of type UHF/2 and GHF/1 and gave a (rather slow) convergence to wave functions of a new type and significantly lower energy. These wave functions are denoted by UHF/3 and GHF/2; they can be considered as combinations of the UHF/2 or GHF/1 wave functions describing the angular ( $\sigma - \pi$ ) correlation and the UHF/1 function describing left-right correlation. Accordingly, as Fig. 1c shows, the UHF/3 and GHF/2 potential curves span an arc between the UHF/2 or GHF/1 curve and the UHF/1.

It should be observed that, above  $R \sim 2.1$  Å, only the UHF/1 solution could be obtained. Similarly, below  $R = 1.82$  Å, the numerical effects cause a "jump" from the UHF/1 branch to the UHF/2 one in the course of the SCF procedure, since UHF/2 has a lower energy at that distance. This means that there is an interval of a length of about 0.2 Å, in which all the six different SCF solutions exist simultaneously. The situation is best characterized by Figs. 2a and 2b, in which the *energy lowering with respect to the RHF method* given by the different UHF and



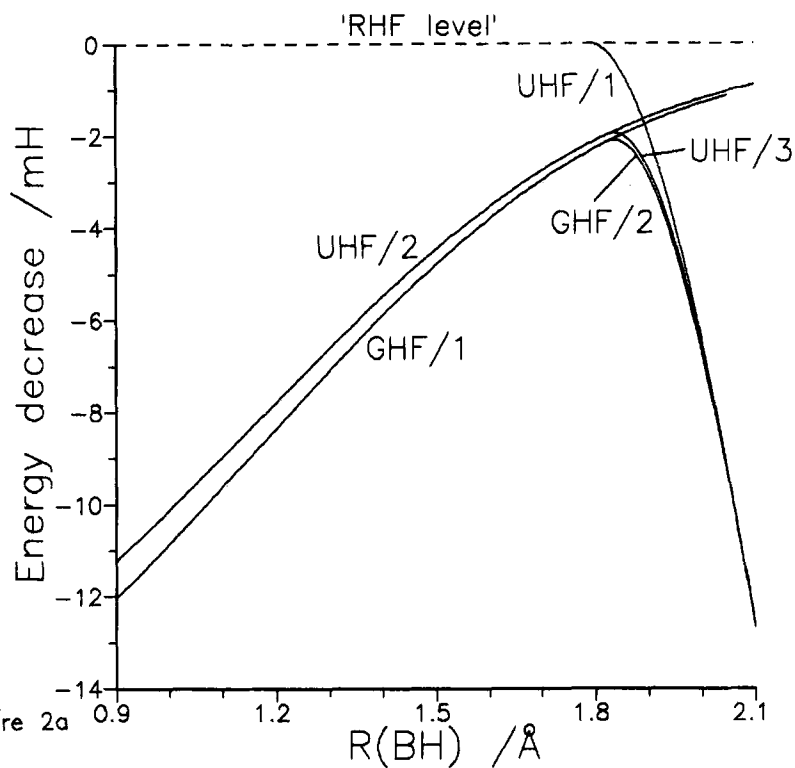


Figure 2a

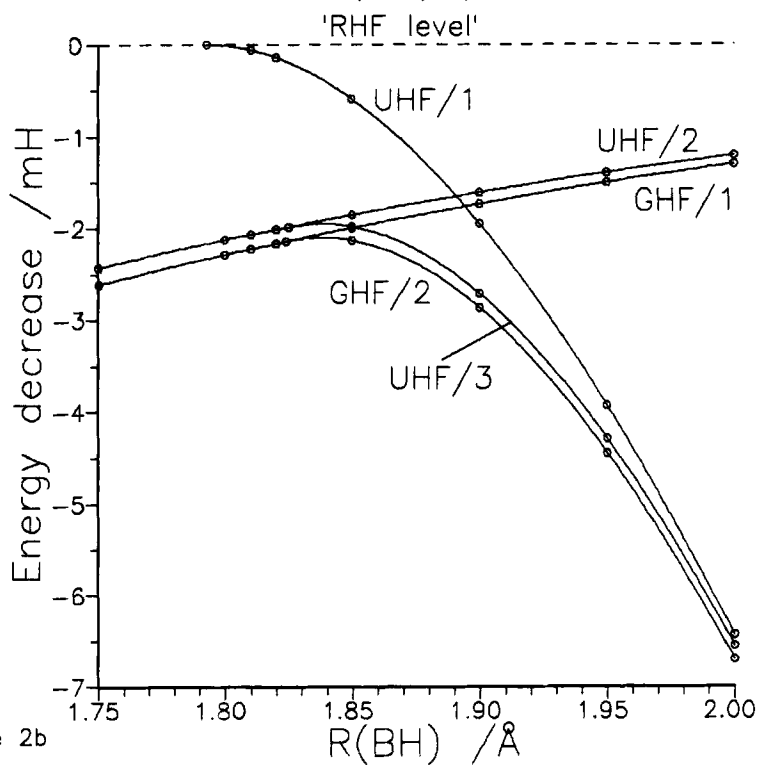


Figure 2b



GHF methods is presented. These curves show rather clearly the characteristics of the different particular solutions obtained.

At the smaller internuclear distances, the UHF and GHF methods give a partial account of the  $\sigma$  -  $\pi$  angular correlation (the UHF/2 and GHF/1 curves), while at the larger distances the left-right correlation described by the UHF/1 solution is the dominating effect. There is a narrow interval where these two effects are of a comparable magnitude: here the "usual" UHF/1 curve crosses the UHF/2 and GHF/1 ones. (This is also the interval in which the short turn on the UHF/1 curve, discussed above, is just started: the importance of the left-right correlation is quickly increasing). The most interesting result is, in our opinion, that there is not only a competition between the effects of angular and left-right correlation, but also that their combination is possible, giving rise to the specific solutions UHF/3 and GHF/2 exhibiting a further energy lowering. This stresses again the mathematical complexity of the Hartree-Fock problem due to the pronounced non-linear character of the general Hartree-Fock equations.

#### 4. A Study of the Hessians in the Hartree-Fock Scheme

The multiplicity of the Hartree-Fock solutions obtained for the BH molecule motivated us to perform a special study to clarify which ones of these solutions correspond to true (local) minima, and which ones correspond to saddle points on the energy hypersurface, and to determine the bifurcation points in which new types of solutions appear as exactly as possible. For that reason we have investigated the Hessians for the RHF, UHF/2 and GHF/1 wave functions discussed above. As is well-known [19,20], the Hessian is defined as a matrix  $\mathbf{H} = \{H_{ij}\}$  with the elements

$$H_{ij} = \partial^2 E / \partial c_i \partial c_j, \quad (4.1)$$

where  $E$  is the total energy and the quantities  $c_i$  are the independent parameters defining the wave function  $\Psi$  under consideration. If all the eigenvalues of  $\mathbf{H}$  are positive, the stationary point considered is a true minimum; if one or more of the eigenvalues are negative, it is a saddle-point. A zero eigenvalue indicates that there exists a parameter, of which the energy is independent at least up to the second order.

In the case of a single determinant wave function, the parameters  $c_i$  above could be, in principle, identified with the

LCAO coefficients of the SCF orbitals involved. However, the invariance of the determinantal wave functions under non-singular linear transformations of the  $N$  basic one-electron functions indicates that the number of really independent parameters is less than that of the LCAO coefficients. Instead of using them, we may utilize a theorem [45] which in the present case can be formulated as follows: the  $N$  not necessarily normalized or orthogonalized one-electron functions  $\psi_i$  in an arbitrary determinantal wave function may be presented by the expression:

$$\psi_i = \psi_i^{\text{occ}} + \sum_p \psi_p^{\text{virt}} \eta_{pi}, \quad (4.2)$$

where  $\psi_i^{\text{occ}}$  and  $\psi_p^{\text{virt}}$  are the occupied and virtual SCF orbitals corresponding to the solution under study, the summation over  $p$  goes from 1 to  $(M-N)$ , and  $M$  is the dimension of the spin-orbital basis used in the calculations. In this case, the expansion coefficients  $\eta_{pi}$  play the role of the independent parameters  $c_i$  used in (4.1).

Even if one starts from SCF estimates of a complex nature, only *real* SCF wave functions have been obtained as a result of the calculations, and this means that both the occupied and virtual SCF orbitals form a real orthonormalized set, spanning the whole subspace of the LCAO basis orbitals, as noted previously. This implies also that all the matrix elements of the Hamiltonian between determinantal wave functions built up from these SCF orbitals are necessarily real. Utilizing this fact, and following the derivation given in [20], the Hessian can be given as

$$\mathbf{H} = \begin{bmatrix} \mathbf{A+B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A-B} \end{bmatrix}, \quad (4.3)$$

where the matrices  $\mathbf{A}$  and  $\mathbf{B}$  are given by the relations

$$A_{ki}^{\text{pr}} = \langle \psi_k^{\text{p}} | H - 1 | \psi_i^{\text{r}} \rangle, \quad B_{ki}^{\text{pr}} = \langle \psi_{ki}^{\text{pr}} | H - 1 | \psi_0 \rangle, \quad (4.4)$$

and the wave functions  $\psi_k^{\text{p}}$  and  $\psi_{ki}^{\text{pr}}$  are determinants which are singly and doubly excited with respect to the SCF determinant  $\Psi_0$ :

$$\psi_k^{\text{p}} = \partial \Psi / \partial \eta_{pk} = \Psi_1(\psi_k^{\text{occ}} \rightarrow \psi_p^{\text{virt}}), \quad (4.5)$$

$$\psi_{ki}^{\text{pr}} = \partial^2 \Psi / \partial \eta_{pk} \partial \eta_{il} = \Psi_2(\psi_k^{\text{occ}} \rightarrow \psi_p^{\text{virt}}, \psi_l^{\text{occ}} \rightarrow \psi_i^{\text{virt}}). \quad (4.6)$$

Here  $\Psi$  is the determinant wave function built up from  $N$  spin-orbitals of type (4.3), and the derivatives are taken in the point  $\Psi = \Psi_0$ , i.e. for all  $\eta_{pk} = 0$ .

The eigenvalue problem of the Hessian matrix  $\mathbf{H}$  factorizes according to (4.3) into the eigenvalue problems for  $\mathbf{A}+\mathbf{B}$  and  $\mathbf{A}-\mathbf{B}$ , the former associated with the stability of  $\Psi_0$  under pure real variations and the latter under pure imaginary ones [20].

The derivation of the explicit formulas and programming of the elements of the matrices  $\mathbf{A} \pm \mathbf{B}$  and their diagonalization was straightforward. The first interesting result obtained was the observation that the lowest eigenvalue of the Hessian in the case of the free Lithium atom is zero. This can easily be understood if one takes into account the fact that the energy of the Li atom in its ground state  $(1s)^2(2s)^1$  is obviously independent of whether the unpaired electron has  $\alpha$  spin or  $\beta$  spin - or a spin quantized along an arbitrary axis in the space.

Similarly, there is at least one zero eigenvalue for the GHF/1 and UHF/2 Hessians studied for the BH molecule, but not for those corresponding to the RHF solution. This is due to the fact that the UHF/2 and GHF/1 wave functions do not have the  $C_\infty$  symmetry of the molecule, but only a (quasi)symmetry of the  $C_{2v}$  type. Therefore, a rotation of the  $\pi$ -contamination (which is added to the  $\sigma$ -orbitals) around the internuclear axis does not change the total energy.

Figs. 3a and 3b show the lowest eigenvalues of the Hessian for the RHF wave function as functions of the internuclear distance. One can see that there is at least one negative eigenvalue at every distance, i.e. the RHF function has a saddle point character everywhere. (The existence of the UHF and GHF solutions with energies lower than the RHF would not necessarily imply that conclusion, since the RHF solution could have, in principle, also a true *local* minimum.) One of the eigenvalues of the Hessian sharply decreases with increasing internuclear distance and at  $R = 1.793 \text{ \AA}$  it crosses the zero level: this is the bifurcation point in which the specific UHF/1 solution is appearing.

The lowest eigenvalues of the Hessian for the UHF/2 wave function are displayed in Figs. 4a and 4b. There is everywhere a negative eigenvalue which can be connected with the existence of the GHF/1 solution with a lower energy. The overall picture is

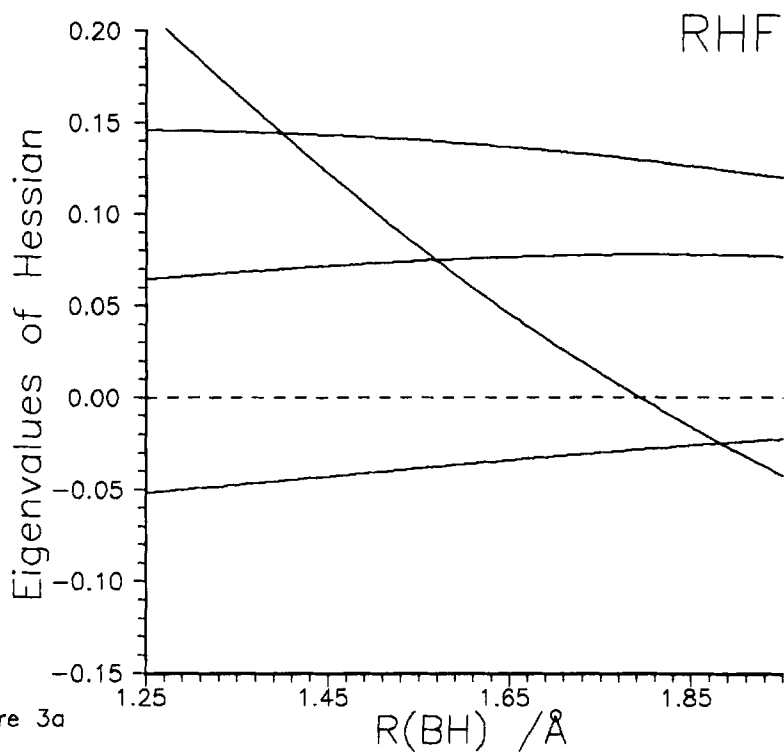


Figure 3a

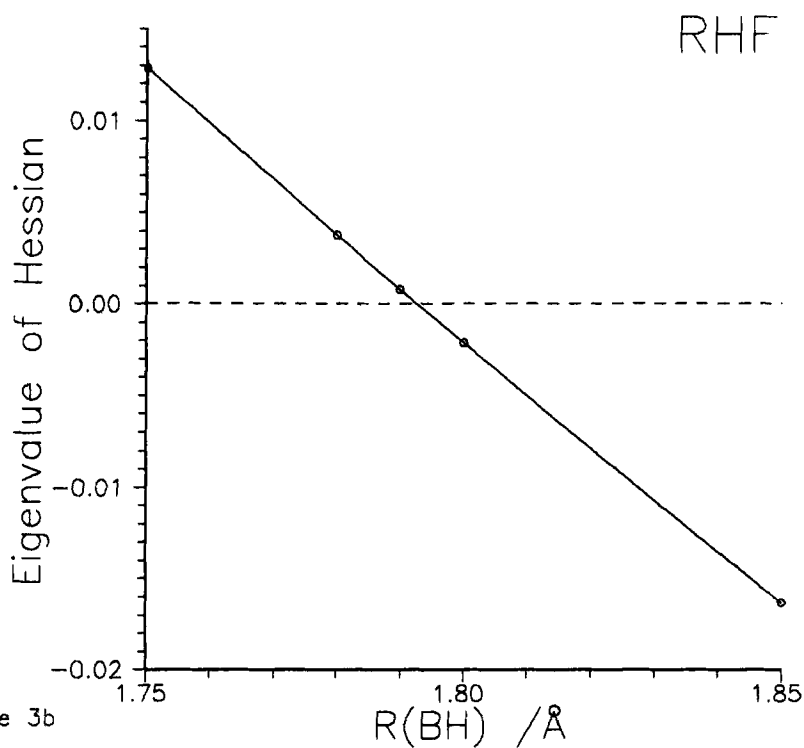


Figure 3b

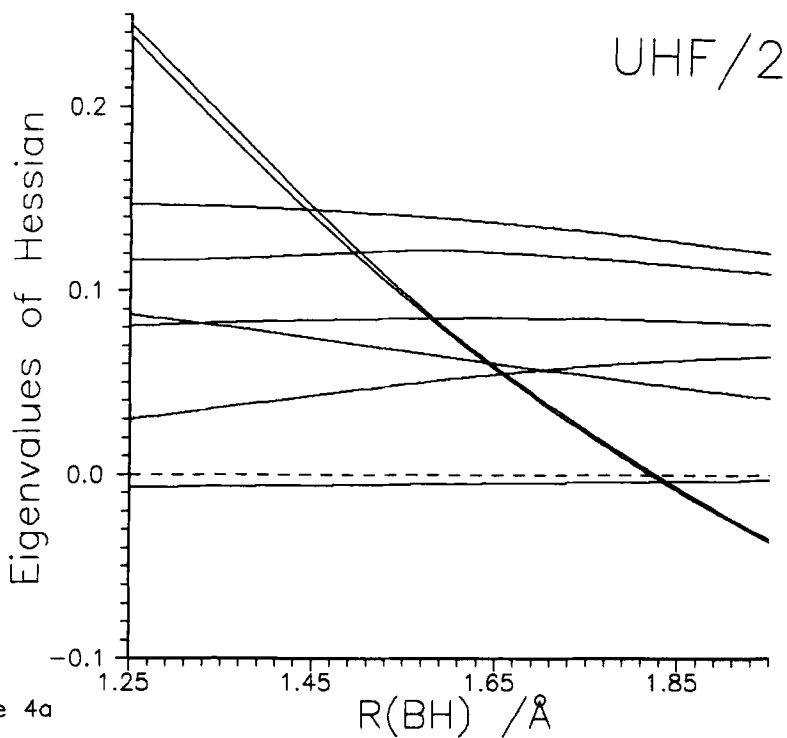


Figure 4a

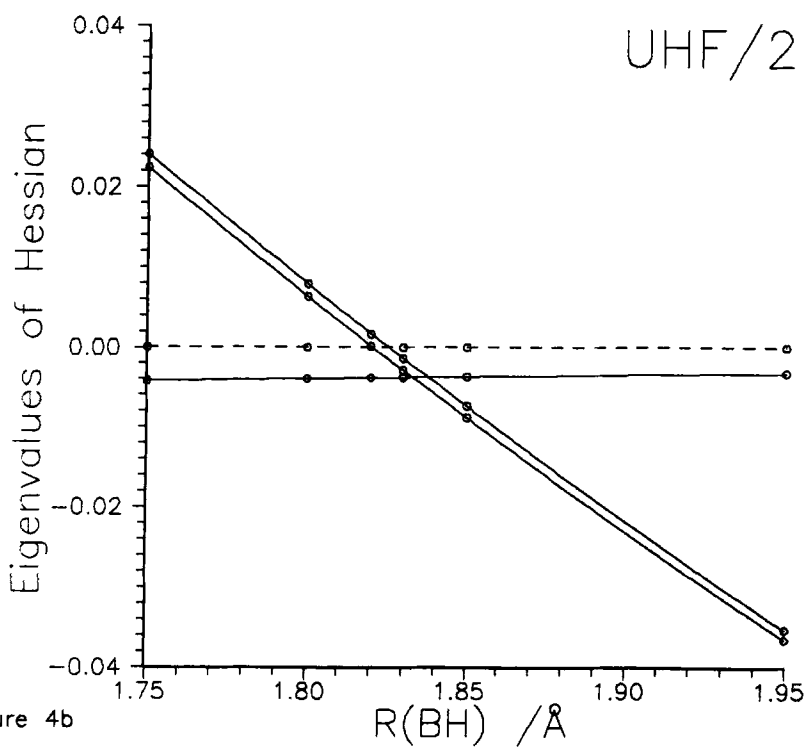


Figure 4b

more complicated than in the RHF case, due to the zero eigenvalue present at all internuclear distances (see above) and to the fact that a pair of close eigenvalues crosses the zero level at  $R \approx 1.82 \text{ \AA}$ . They are related to the appearance of a pair of new solution UHF/3 and GHF/2 around this point.

The lowest eigenvalues of the Hessian for the GHF/1 solution are depicted in Figs. 5a and 5b. The picture is now somewhat simpler: there is a zero eigenvalue at all distances, connected with the rotational arbitrariness mentioned above, but there is no negative eigenvalue until  $R \approx 1.824 \text{ \AA}$ , which is the point where the GHF/2 solution starts to exist.

In the case of the RHF and UHF/2 wave functions, the matrix  $\mathbf{A-B}$  does not have any eigenvalues which are not present also for the matrix  $\mathbf{A+B}$ ; only the degrees of degeneracy may be different. However, for the GHF/1 Hessian no such coincidence of eigenvalues is present. Moreover, the eigenvalues of the matrix  $\mathbf{A-B}$  crosses the zero level at a point about a thousand of an  $\text{\AA}$  prior to the eigenvalues of the matrix  $\mathbf{A+B}$ . Based on this observation, we have tried to find a further, *substantially complex*, solution to the GHF equations, utilizing the corresponding eigenvector of the Hessian for this purpose. This attempt was unsuccessful with the computational tools we had available; nevertheless, one cannot exclude the existence of such a seventh solution of the GHF equations. We may suppose, however, that even if such a solution does exist mathematically, one may have to go to much higher numerical accuracy to be able to distinguish it from the GHF/2 solution.

Our little study shows as a side result that, in the solution of the SCF problem at any level, it is essential to understand in much greater detail the problem *of the connection between the starting point of the SCF procedure and the final SCF solution* than we do today. In our opinion, it would hence be worthwhile to devote much more research to this problem - both mathematically and numerically.

## 5. Concluding Remarks

In this paper we have studied the original Hartree-Fock method - here referred as the GHF-scheme - for some simple atomic and molecular systems by using general spin-orbitals (1.7) of a complex character, and we have found that there exist GHF-solutions of TSDW type which give lower energies  $\langle H \rangle$  than the RHF- and UHF-schemes, but also that quite a few SCF solutions of different type may exist simultaneously. The purpose of the

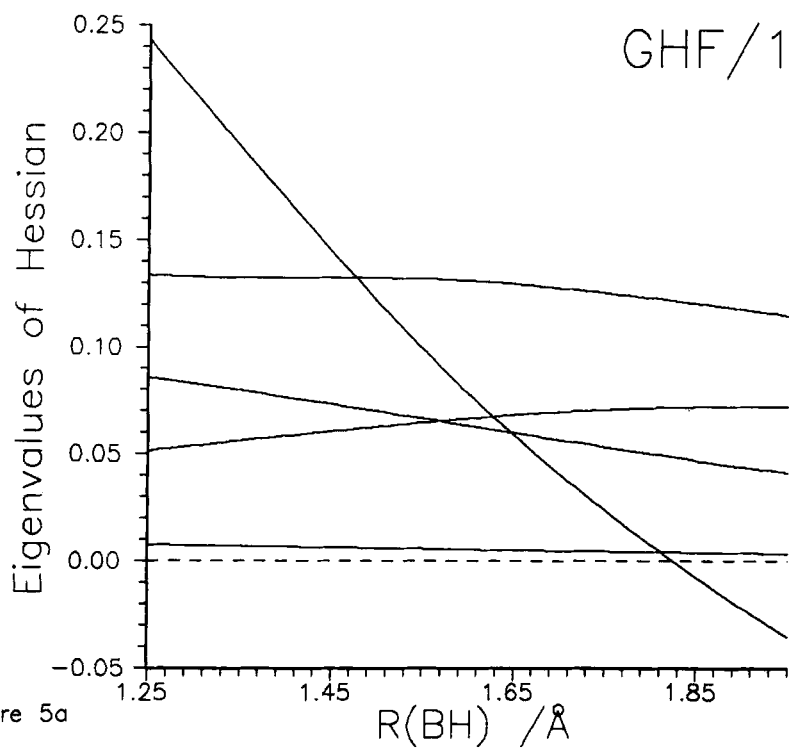


Figure 5a

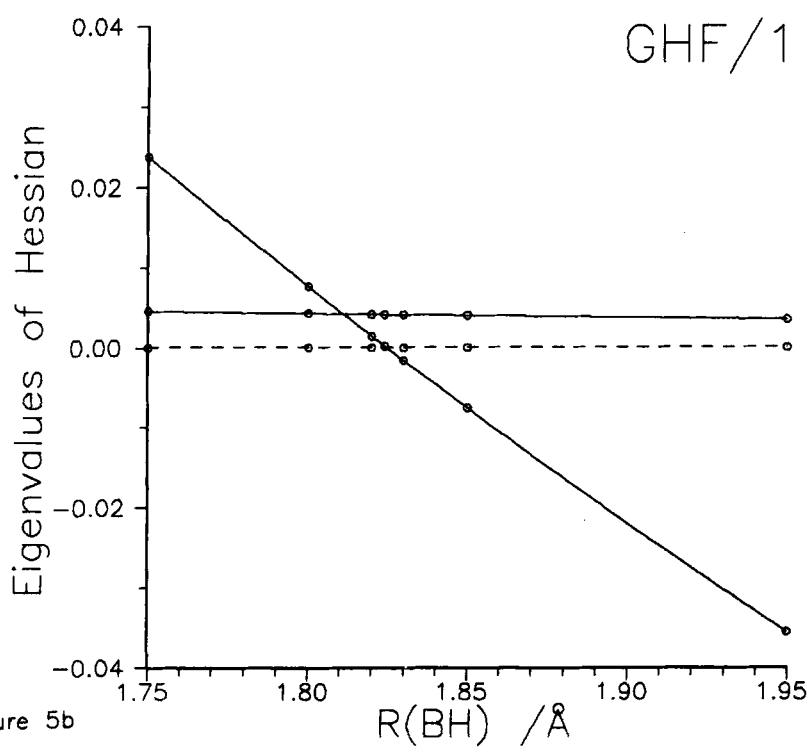


Figure 5b

study is, of course, to find the *absolute minimum*  $\langle H \rangle$  for the energy on the hypersurface associated with the SCF procedure. At the same time it should be observed that, whenever such an absolute minimum is found, the associated Slater determinant  $D$  is usually a *mixture* of different symmetry types. It is true that by means of the symmetry projectors  $Q_k$  forming a resolution of the identity  $1 = \sum_k Q_k$ , one may carry out a unique component analysis of the Slater determinant  $D$ :

$$D = 1.D = (\sum_k Q_k)D = \sum_k Q_k D = \sum_k D_k, \quad (5.1)$$

where the component  $D_k = Q_k D$  has the correct symmetry properties. It is also clear that this component does not have an optimal energy  $\langle H \rangle_k$ , since one has varied before the projection, and that - if one want to preserve the correct symmetry property - one ought to take the projection before the variation. In this way one is naturally lead to the Projected Hartree-Fock (PHF) scheme [46], which preserves many of the fundamental features of the independent-particle-model. So far, the PHF-scheme has in the DODS- and AMO-methods [47] been developed essentially as an extension of the UHF-scheme, but it is obvious that one could get an even better treatment of the correlation problem, if one could take the projection of a Slater determinant built up from *general spin-orbitals*. It has been shown [48] that, even for two-electron systems, the PHF scheme gives a lower energy when one is using general spin-orbitals (GSO's) and that the same is true also for the lithium atom [49] with  $N = 3$ . So far it has not been easy to carry out an extension of the PHF-scheme using complex GSO's to many-electron systems. In such a case, it is certainly important to learn how to handle determinants built up from complex general spin-orbitals, and it is hence hoped that the study in this paper will be of value not only as an exposé of the GHF method but also as a first step towards an extension of the PHF-sceme.

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