

Some comments on the general Hartree–Fock method

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A study is made of the general Hartree–Fock (GHF) method, in which the basic spin-orbitals may be mixtures of functions having α and β spins. The existence of the solutions to the GHF equations has been proven by Lieb and Simon, and the nature of the various types of solutions has been group theoretically classified by Fukutome. Some numerical applications using Gaussian bases are carried out for some simple systems: the beryllium and carbon atoms and the BH molecule. Some GHF solutions of the general Fukutome-type “torsional spin density waves” (TSDW) were found.

The independent-particle model (IPM) in which each particle moves under the influence of the outer potential and the average potential of all the other particles in the system, has had its most successful formulation in the modern quantum theory of the electronic structure of atoms, molecules, and crystals in the form of the Hartree–Fock (HF) scheme [1]. In this approach, the total wavefunction for a N -electron system is approximated by a single Slater determinant, built up from N spin-orbitals $\psi_k(x)$ with $x = (r, \zeta)$ having the general form

$$\psi_k(x) = \psi_k(r, \zeta) = u_k(r)\alpha(\zeta) + v_k(r)\beta(\zeta). \quad (1)$$

By starting from the Hamiltonian H for the many-electron system and applying the variation principle $\delta\langle H \rangle = 0$, one could derive the equations for the optimum choice of the spin-orbitals:

$$F(1)\psi_k(x_1) = \sum_I \psi_I(x_1)\lambda_{Ik}, \quad (2)$$

which have become known as the Hartree–Fock (HF) equations. Slater had pointed out that – except for an irrelevant factor – the determinant D is invariant under a nonsingular 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, and that this set without loss of generality may be chosen orthonormal. The Lagrangian multipliers λ_{Ik} form a Hermitian matrix $\lambda = \{\lambda_{Ik}\}$, and it could then be shown that the eq. (2) could be brought by a unitary transformation to the simple form

$$F(1)\psi_k(x_1) = \epsilon_k \psi_k(x_1), \quad (3)$$

where the eigenvalues ϵ_k were interpreted as one-electron energies. There are different types of solutions for various types of Lagrangian multipliers $\lambda = \{\lambda_{Ik}\}$ – some are for instance localized – and it should be observed that the so-called *canonical Hartree–Fock functions* defined by (3) are always linear combinations of the other solutions. The effective Hamiltonian $F(1)$ is often referred to 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 are described by the density matrix

$$\rho(x_1, x_2) = \sum_k \psi_k(x_1)\psi_k^*(x_2), \quad (4)$$

where $\rho(x_1, x_2)$ is the kernel of an operator $\rho = |\psi\rangle\langle\psi|$ having the properties

$$\rho^2 = \rho, \quad \rho^\dagger = \rho, \quad \text{Tr} \rho = N. \quad (5)$$

The properties of the Hartree–Fock scheme were further investigated by Dirac [2], who showed that

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the Fock operator may be represented in the simple form

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

$$= H_1 + J_1 - K_1, \quad (6)$$

$$H_1 = p_1^2/2m - e^2 \sum_g Z_g/r_{1g}, \quad (7)$$

$$J_1 = e^2 \int dx_2 \frac{\rho(2, 2)}{r_{12}},$$

$$K_1 = e^2 \int dx_2 \frac{\rho(1, 2)P_{12}}{r_{12}}, \quad (8)$$

where J_1 and K_1 are referred to as the Coulomb and exchange operators in the Hartree-Fock scheme, and P_{12} is a permutation or exchange operator defined through the relation $P_{12}u(1) = u(2)$. 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 ρ is the projector on the subspace spanned by the N one-electron functions. The one-electron energies ϵ_k have finally been given a simple physical interpretation by Koopmans [3].

The canonical Hartree-Fock equations (3) are a system of rather complicated non-linear integro-differential equations combined with an eigenvalue problem, and – following an idea by Hartree – they were usually solved by an iterative process until there were no more changes in the significant figures, and the solutions become *self-consistent*. Even today little is known whether this self-consistent-field (SCF) procedure is mathematically convergent or not.

In the quantum theory of atoms, molecules, and crystals, symmetry properties of the many-electron Hamiltonian H are of fundamental importance, and in the applications of the HF scheme it was from the very beginning assumed that these symmetry properties would be reflected in eqs. (3), particularly since it had been shown that such an assumption would be self-consistent [4]. In view of later experiences, this approach is today known as the *restricted Hartree-Fock* (RHF) scheme. In the 1950s it was found that, if one lifted some of these symmetry restrictions and

developed an *unrestricted Hartree-Fock* (UHF) scheme, one may obtain lower energies than before [5]. In 1963, the occurrence of a *symmetry dilemma* [6] in the Hartree-Fock method was pointed out. It implied 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 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 [7] in the current literature.

Even in the UHF scheme, one assumed as a rule that the basic one-electron functions would be of pure α or β type, whereas it is evident that the most general form would be a mixture of type (1) corresponding to a *general Hartree-Fock* (GHF) scheme, and that such a scheme would be identical to the original HF scheme if one avoids any additional symmetry assumptions. In solid-state theory, Overhauser [8]^{#1} found that such mixtures would have a lower energy than the plane waves, and one became interested in *spin-density waves* (SDW) and *charge-density waves* (CDW).

The general Hartree-Fock equations (3) 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 [10] 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 pro-

^{#1} For a survey of some applications to solid-state theory, see e.g. ref. [9].

cedure is an iterative procedure which is subject to the laws discovered by Schröder [11] (see also ref. [12], particularly Appendix A) in 1870, which may be used to speed up the convergence or to change an obviously divergent process into a convergent one.

A tremendous step forward was taken when Fukutome [13] starting in 1968 discovered that the Fock operator (6) has certain intrinsic symmetry properties, which make it possible to classify the solutions to the general Hartree-Fock equations into *eight different classes* by means of group theory, and that this classification scheme applies both to nuclear physics and the electronic structure of matter. To describe the solutions he 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), and torsional spin density waves (TSDW). In a study of the properties of the polyacetylenes by means of the Pariser-Parr-Pople (PPP) approximation, Fukutome [14] showed that this scheme could be applied successfully to molecular systems.

The authors were interested in making some exploratory *ab initio calculations* to some small atomic and molecular systems in order to get some experience in solving the GHF equations. It is somewhat remarkable that the solution of the GHF equations follows the same lines as the solution of the standard RHF or UHF equations, except that one has now twice as many orbitals as before and that they may be of complex character. Substituting the relation $\psi = u\alpha + v\beta$ into the formula $\rho = |\psi\rangle\langle\psi|$, one gets

$$\rho = \rho^{++}\alpha\alpha + \rho^{+-}\alpha\beta + \rho^{-+}\beta\alpha + \rho^{--}\beta\beta, \quad (9)$$

where one is now dealing with four space components of the density matrix. For the Coulomb operator J_1 defined by (8), one gets in particular

$$J_1 = e^2 \int d\mathbf{r}_2 \frac{\rho^{++}(2,2) + \rho^{--}(2,2)}{r_{12}}, \quad (10)$$

whereas for the exchange operator K_1 it is convenient to introduce the four components

$$K_1^{\mu\nu} = e^2 \int d\mathbf{r}_2 \frac{\rho^{\mu\nu}(1,2)P_{12}^{\nu\mu}}{r_{12}}, \quad (11)$$

where $\mu, \nu = +, -$, and the permutation operator P_{12} works only on the orbital coordinates. In studying the Hartree-Fock equations (3) in the condensed form $F(1)\psi = \psi\epsilon$, where ϵ is the diagonal matrix formed by the eigenvalues ϵ_k , one can now easily separate the α and β components, and using (10) and (11), one obtains directly

$$\begin{aligned} & \begin{Bmatrix} H_1 + J_1 - K_1^{++} & -K_1^{+-} \\ -K_1^{-+} & H_1 + J_1 - K_1^{--} \end{Bmatrix} \begin{Bmatrix} u(1) \\ v(1) \end{Bmatrix} \\ & = \begin{Bmatrix} u(1) \\ v(1) \end{Bmatrix} \epsilon. \end{aligned} \quad (12)$$

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. These equations are then easily generalized to the MO-LCAO approach or to any approximate method using a finite basis.

Since the general spin-orbitals (GSOs) of type (1) 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 [15]. Applications to some two-electron systems – the helium-like ions and the hydrogen molecule – by Lunell (see ref. [16], particularly p. 96 and ref. [17], particularly p. 495) showed, however, that the GHF scheme converged to exactly the same energy as the UHF scheme. Physically this probably depends 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.

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. In Fukutome's terminology, the GHF solution was a torsional spin density wave (TSDW).

Table 1
Energies of the Be Atom calculated using a STO-6G basis set

Wavefunction	Energy (au)
RHF	-14.503361
UHF ($S_z=0$)	-14.505074
GHF (TSDW)	-14.505190
triplet (UHF, $S_z=1$)	-14.442082
singlet $(1s)^2(2p)^2$	-14.172547

Table 2
Energies of the carbon atom calculated using 4-31G and 6-31G basis sets

Wavefunction	Energies (au)	
	4-31G	6-31G
RHF	-37.544557	-37.588204
UHF ($S_z=0$)	-37.60405	-37.647030
GHF	-37.61263	-37.655524
triplet (UHF, $S_z=1$)	-37.63505	-37.677837

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 wavefunction 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 Fukutome's terminology, the GHF solution was again a torsional spin density wave (TSDW). 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 performed. This molecule is a very interesting species: it is a closed-shell σ -system which

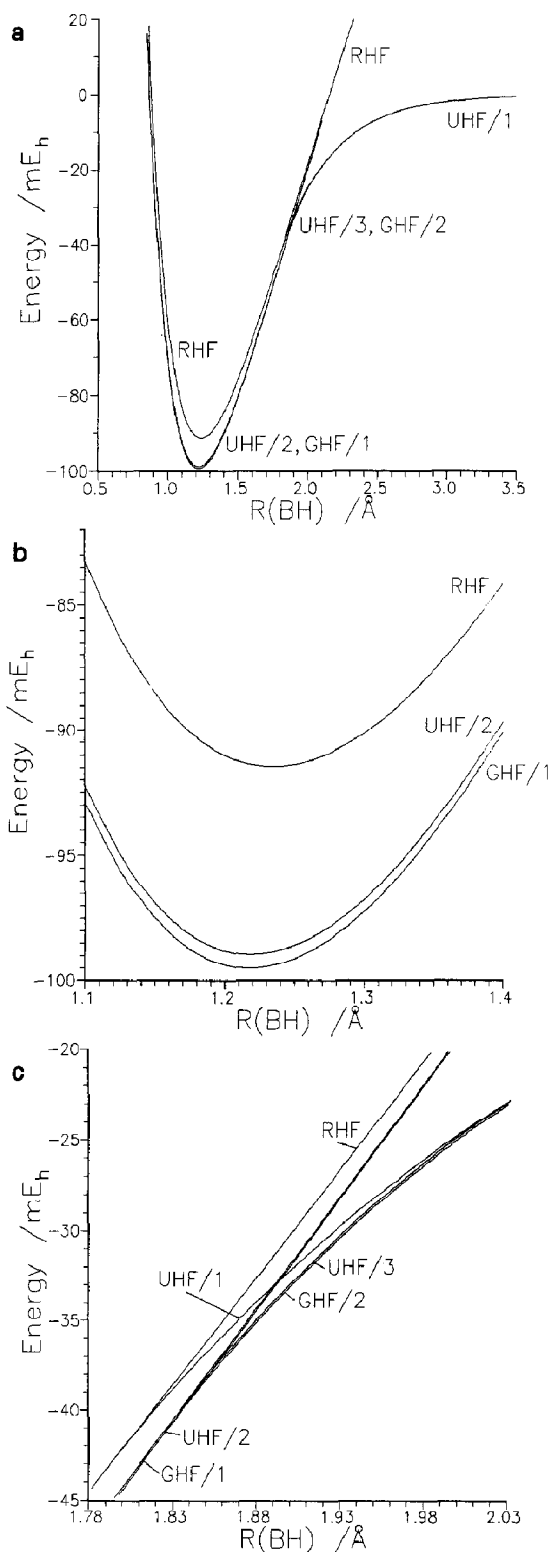


Fig. 1.

is, at the same time, paramagnetic. In the RHF or conventional (spin-unrestricted) UHF approaches, all the π -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 π -levels. The results are illustrated in figs. 1a and 1b.

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; see fig. 1c.

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 some of the RHF, UHF and GHF wavefunctions mentioned above. As is well-known [7], the Hessian is defined as a matrix $\mathbf{H} = \{H_{ij}\}$ with the elements

$$H_{ij} = \partial^2 E / \partial c_i \partial c_j, \quad (13)$$

where E is the total energy and the quantities c_i are the independent parameters defining the wavefunction Ψ 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. We note that, so far, one has no criterion for the existence of an *absolute minimum*. All the results of the studies of the Hessians agree completely with the bifurcation points of the energy curves for the various solutions, and they give further valuable additional information about the nature of the solutions. Some numerical results for the BH molecule are given in tables 3–5.

Table 3

Four lowest eigenvalues of the Hessian for the RHF solution of the B–H molecule ^{a)}

R (Å)	Eigenvalues of Hessian			
1.25	-0.05184	0.06456	0.14580	0.21050
1.3	-0.04970	0.06639	0.14541	0.18786
1.4	-0.04529	0.06992	0.14406	0.14339
1.5	-0.04079	0.07303	0.14179	0.10150
1.6	-0.03632	0.07548	0.13848	0.06319
1.65	-0.03415	0.07639	0.13642	0.04547
1.7	-0.03202	0.07705	0.13412	0.02871
1.75	-0.02997	0.07747	0.13158	0.01285
1.78	-0.02877	0.07760	0.12995	0.00375
1.79	-0.02838	0.07762	0.12939	0.00078
1.8	-0.02799	0.07763	0.12882	-0.00215
1.85	-0.02610	0.07752	0.12586	-0.01634
1.95	-0.02259	0.07652	0.11946	-0.04251

^{a)} One eigenvalue becomes negative at a “branching” or “critical” point.

Table 4

Some lowest eigenvalues of the Hessian for the usual UHF (DODS) solution of the B–H molecule ^{a)}

R (Å)	Eigenvalues of Hessian					
1.25	-0.00705	0.02991	0.08076	0.08688	0.23784	0.24419
1.4	-0.00620	0.03968	0.08332	0.07749	0.16368	0.16983
1.6	-0.00504	0.05191	0.08519	0.06394	0.07644	0.07786
1.75	-0.00420	0.05903	0.08491	0.05384	0.02232	0.02399
1.8	-0.00394	0.06083	0.08441	0.05061	0.0063	0.00787
1.82	-0.00384	0.06147	0.08415	0.04934	0.00015	0.00167
1.83	-0.00379	0.06176	0.08400	0.04871	-0.00287	-0.00137
1.85	-0.00369	0.06231	0.08369	0.04747	-0.00881	-0.00736
1.95	-0.00322	0.06424	0.08162	0.04151	-0.03653	-0.03532

^{a)} This solution is denoted UHF/2 on fig. 1. The table contains the four eigenvalues of the Hessian which are the lowest ones at the smaller internuclear distances and two which become negative around $R = 1.82$ Å (“branching” or “critical” point).

Table 5
Six lowest eigenvalues of the Hessian for the GHF solution of the B-H molecule ^{a)}

R (Å)	Eigenvalues of Hessian					
1.25	0.00000	0.00757	0.05141	0.08557	0.13345	0.24275
1.4	0.00000	0.00666	0.05847	0.07646	0.13220	0.16852
1.6	0.00000	0.00542	0.06660	0.06325	0.13102	0.07808
1.75	0.00000	0.00452	0.07076	0.05334	0.12534	0.02373
1.8	0.00000	0.00424	0.07158	0.05016	0.12304	0.00761
1.82	0.00000	0.00414	0.07183	0.04892	0.12206	0.00142
1.824	0.00000	0.00411	0.07187	0.04867	0.12186	0.00020
1.83	0.00000	0.00408	0.07194	0.04830	0.12156	-0.00162
1.85	0.00000	0.00398	0.07211	0.04708	0.12054	-0.00760
1.95	0.00000	0.00348	0.07231	0.04124	0.11500	-0.03553

^{a)} This solution is denoted GHF/1 on fig. 1. One eigenvalue becomes negative at a "branching" or "critical" point.

Our study shows as a side results 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 be worthwhile to devote more research to this problem – both mathematically and numerically.

The results reported in this Letter are of a preliminary nature. A much more detailed description of the work connected with this Letter is given in ref. [18]. It contains a more extensive review of the history of the Hartree-Fock scheme including references, as well as an outline of the numerical work, and an illustration of the results in the form of numerous graphs. It is also hoped that the experiences we have gained in this work will be of value in studying the projected Hartree-Fock (PHF) method based on general spin-orbitals of type (1).

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