Theoret. Chim. Acta (Ber.) 41, 279–285 (1976)

The Half-Projected Hartree-Fock Method

II. Results for Some Small Molecules and Some Symmetry Considerations

P. Anthony Cox and Melvyn H. Wood

Institut de Chimie, Université Louis Pasteur, Strasbourg, France

Received June 18, 1975/December 3, 1975

Solutions of the half-projected Hartree-Fock equations, given in a previous paper, have been obtained for some small molecules containing first-row atoms. In many cases, it is possible to find several solutions, the existence of which can be explained by symmetry arguments.

Key words: Hartree-Fock method, half-projected ~ – Half-projected Hartree-Fock method – H_2O – CO

1. Introduction

In order to introduce more flexibility into the usual one-determinant restricted Hartree-Fock (RHF) method, it has been suggested that the electrons of opposite spin be assigned to spatially different orbitals [1, 2], giving rise to the unrestricted Hartree-Fock (UHF) function:

$$\Psi = |a_1 \bar{b}_1 a_2 \bar{b}_2 \dots a_N \bar{b}_N|. \tag{1}$$

However, this function is not a spin eigenfunction and often the best orbitals, found by minimizing the total energy, are found to be RHF orbitals. To remedy these deficiencies of the UHF method, Löwdin [3] has suggested projecting the UHF function to give a spin eigenfunction of the desired multiplicity, the resulting function being known as the projected Hartree-Fock (PHF) function. Unfortunately, this method, which has been applied only to very small systems [4–8], becomes far too complex for larger systems due to the large numbers of Slater determinants involved in the PHF function. Another two-determinantal function has been suggested by Smeyers and Doreste-Suarez [8]. This function given by

$$\Psi = |a_1 \bar{b}_1 a_2 \bar{b}_2 \dots a_N \bar{b}_N| + |b_1 \bar{a}_1 b_2 \bar{a}_2 \dots b_N \bar{a}_N| \tag{2}$$

has been shown to contain only states with even spin quantum number, and is called the half-projected Hartree-Fock (HPHF) function since it may be expressed as the UHF function, Eq.(1), projected on the subspace with even spin quantum number [8]. We have recently shown [9] that it is possible to obtain the optimum orbitals for the HPHF function by the iterative solution of two eigenvalue problems in the same manner as the normal UHF method, and have written a computer program to do so. We have also shown [9] how it is possible to obtain the expectation value of the total spin operator ($\langle \mathscr{S}^2 \rangle$), and the natural orbitals (NO) for the function. The NOs, which occur in pairs whose occupation numbers add to 2, may be expressed in terms of the corresponding orbitals which have the property [2, 9]

$$\langle a_i | b_j \rangle = \lambda_i \delta_{ij}. \tag{3}$$

Thus, for NO's χ and η we have

$$\begin{aligned} |\chi\rangle &= |a_i\rangle + |b_i\rangle \\ |\eta\rangle &= |a_i\rangle - |b_i\rangle. \end{aligned} \tag{4}$$

In this paper we present the results of HPHF calculations performed on some small molecules containing first row atoms, using a minimal basis of Slater orbitals, each orbital being expanded in terms of four Gaussian functions [10]. The role of symmetry is discussed in some detail with reference to the results obtained.

It may be noted at this point that the starting orbitals $\{a\}$ and $\{b\}$, for our HPHF calculations are taken to be the RHF orbitals, one or more of the occupied orbitals (c_i) having been perturbed by mixing with one or more of the virtual orbitals (c_k) according to

$$\begin{aligned} |a_i\rangle &= |c_i\rangle + \sum p_{ik} |c_k\rangle \\ |b_i\rangle &= |c_i\rangle - \sum p_{ik} |c_k\rangle. \end{aligned} \tag{5}$$

where the p_{ik} are mixing coefficients, usually having the value 0.2.

2. Results

2.1. Water

Four solutions have been obtained for this molecule. Table 1 gives the atomic co-ordinates, initial orbital mixing, total energies and $\langle \mathscr{S}^2 \rangle$ values for the four calculations, the correlation energies (CE) obtained being 0.57, 0.53, 0.38 and 0.03 eV respectively. These may be compared with an estimated CE of 9.90 eV [11]. For all the solutions $\langle \mathscr{S}^2 \rangle$ is found to be small. In Table 2 we give the NO's

Table 1. Initial orbital mixing and calculated total energies and expectation values of $\mathscr{S}^2$ for H_2O[a]

Calculation Number	Orbitals Mixed	Total Energy (a.u.)	$\langle \mathscr{S}^2 \rangle$
1	extensive	−75.5177	0.006
2	$3a_1 - 4a_1$	−75.5160	0.034
3	$3a_1 - 2b_2$	−75.5106	0.027
4	$1b_1 - 4a_1$	−75.4979	0.000

[a] The co-ordinates, in bohr, are H1 (−1.1073, 1.4301, 0.0); H2 (−1.1073, −1.4301, 0.0); O (0.0, 0.0, 0.0) and the RHF energy is −75.4967 a.u.

Table 2. Natural orbitals obtained from calculations on H_2O

Calculation Number	N.O. Occupation Number	λ Value for Corresponding Orbitals	Atomic Orbital Coefficients						
			H1(1*s*)	H2(1*s*)	O(1*s*)	O(2*s*)	O($2p_x$)	O($2p_y$)	O($2p_z$)
1	1.999	0.993	0.52	−0.05	−0.06	0.15	−0.49	0.40	–
	1.976	0.807	0.12	−0.55	0.02	0.01	0.48	0.46	–
	0.024	0.807	−0.05	1.16	0.09	−0.61	0.52	0.71	–
	0.001	0.993	−1.16	0.01	−0.09	0.64	−0.54	0.68	–
2	1.989	0.933	0.32	0.32	−0.04	0.02	−0.72	–	–
	1.984	0.883	−0.44	0.44	–	–	–	−0.61	–
	0.016	0.883	0.84	−0.84	–	–	–	−0.99	–
	0.011	0.933	0.80	0.80	0.12	−0.88	0.75	–	–
3	1.991	0.933	0.32	0.32	−0.01	−0.15	−0.76	–	–
	1.989	0.906	−0.44	0.44	–	–	–	−0.61	–
	0.011	0.906	−0.80	−0.80	−0.12	0.88	−0.75	–	–
	0.009	0.933	0.84	−0.84	–	–	–	−0.99	–
4	1.998	0.937	–	–	–	–	–	–	1.00
	0.002	0.937	0.80	0.80	0.12	−0.88	0.74	–	–

with occupation numbers different from 2, from which it is possible to obtain the corresponding orbitals if desired, using Eq.(4). The NO's resulting from calculation (1) are not symmetry orbitals whereas those from the other three calculations are. Thus the lowest energy HPHF solution for H_2O yields non-symmetry NO's. It is also the solution with the least spin contamination, and corresponds to the situation where most of the observed *CE* is obtained from a single O–H bond. Solution (2) gives equal correlation in both of the O–H bonds simultaneously, the essentially RHF $1b_2$ orbital being correlated by another b_2 orbital. The main correlation in solution (3) arises from the correlation of the essentially RHF $1b_2$ orbital by an orbital of a_1 symmetry, yielding correlation across the *xz* plane. The fourth calculation yields correlation out of the molecular plane, where the $1b_1$ RHF orbital is correlated by an a_1 orbital. This type of correlation is obviously not well recovered when a minimal basis set is used since there is only one atomic orbital combination of b_1 symmetry.

2.2. *Carbon Monoxide*

The results obtained for CO are given in Table 3, the bond length chosen for the calculations being 2.13 bohr. Table 3 gives the initial orbital mixing and calculated total energies and $\langle \mathcal{S}^2 \rangle$ values for the four solutions obtained, the calculated *CE*'s being 0.27, 0.45, 0.78 and 0.82 eV respectively. Once again no serious spin contamination is noted in the solutions. Solution (1) gives correlation of the lone pair electrons, the essentially RHF 5σ orbital being correlated by a single π-type orbital. The other three solutions give π-electron correlation, the first two yielding symmetry NO's with the third, which gives the maximum *CE*, yielding non-symmetry orbitals. Solutions (2) and (3) both give equal amounts of correlation in the two π-orbitals. However, reference to the corresponding orbitals shows that in solution (3) both orbitals of the $\{a\}$ set are localised on one atom,

Table 3. Initial orbital mixing and calculated total energies and expectation values of $\mathscr{S}^2$ for CO[a]

Calculation Number	Orbitals Mixed	Total Energy (a.u.)	$\langle \mathscr{S}^2 \rangle$
1	$5\sigma - 2\pi x$	-112.0373	0.018
2	$1\pi x - 2\pi y$	-112.0437	0.051
3	$4\sigma - 6\sigma$	-112.0557	0.093
4	extensive	-112.0571	0.033

[a] The RHF energy is -112.0271 a.u.

and both $\{b\}$ orbitals on the other atom, whereas in solution (2) the two $\{a\}$ orbitals are localised one on each atom, and similarly for the $\{b\}$ orbitals. Thus solution (3) yields the lower energy due to the more favourable exchange energy. In solution (4) the *CE* gained is concentrated in one of the π directions, there thus exists a plane of symmetry for the NO's in this case.

2.3. *Ammonia and Methane*

Two solutions have been obtained for NH_3 which differ in energy by about 0.01 eV only. The lowest energy solution has non-symmetry NO's and corresponds to the situation where correlation in one N–H bond is higher than in the other two. The higher energy solution which has symmetry NO's gives a *CE* of 0.50 eV and $\langle \mathscr{S}^2 \rangle$ value of 0.042.

In the case of CH_4 we have obtained only one solution, which give symmetry NO's, a *CE* of 0.54 eV, and $\langle \mathscr{S}^2 \rangle$ value of 0.053.

3. Discussion

The existence of multiple HPHF solutions may be understood in terms of the symmetry of the molecule. Let us write the HPHF function of Eq.(2) in the form:

$$\Psi = \mathscr{A}[\Psi_a \bar{\Psi}_b + \Psi_b \bar{\Psi}_a]. \tag{6}$$

Here Ψ_a and Ψ_b represent Slater determinants of N electrons in the sets of orbitals $\{a\}$ and $\{b\}$ respectively, the bar indicates that all electrons have beta spin, and $\mathscr{A}$ completes the antisymmetrisation of all $2N$ electrons. We also define the functions ϕ_1 and ϕ_2 from:

$$\Psi_a = \phi_1 + \phi_2 \tag{7a}$$

$$\Psi_b = \phi_1 - \phi_2. \tag{7b}$$

In the starting orbitals, formed from the RHF solution according to Eq.(5), the functions ϕ_1 and ϕ_2 have symmetry properties determined by the symmetries of the orbitals i and k which are mixed. It is convenient to distinguish four possibilities:

(I) If i and k are non-degenerate orbitals of the same symmetry, ϕ_1 and ϕ_2 will both be totally symmetric. The $\{a\}$ and $\{b\}$ orbitals will both be sets of symmetry orbitals, and the HPHF wavefunction will have the full symmetry of the molecule.

(II) If *i* and *k* are non-degenerate orbitals of different symmetry, ϕ_1 will be totally symmetric, and ϕ_2 will transform according to the (non-degenerate) direct product of the irreducible representations (IR) of *i* and *k*. The individual orbitals will not be symmetry orbitals, but the $\{a\}$ and $\{b\}$ sets will be related by some operation of the molecular point-group, and so (unlike type (I)), will have the same set of HPHF eigenvalues. Reconstructing the HPHF wavefunction in Eq.(6), we find only the direct products of ϕ_1 with itself and ϕ_2 with itself, and so the full wavefunction is totally symmetrical.

(III) If *i* and *k* are of different symmetry, but one or both of them belong to degenerate IR's, the situation resembles (II), except that ϕ_2 will now transform according to a degenerate, and possible reducible, representation. Thus the HPHF wavefunction will contain non-totally-symmetric components, and will not transform into itself under all the operations of the point-group.

(IV) With an extensive mixing of different sets of orbitals *i* and *k* of different symmetries, ϕ_1 and ϕ_2 may both be non-symmetrical. In this case the $\{a\}$ and $\{b\}$ sets will not be symmetry orbitals, nor will they be related by any symmetry operation. The HPHF wavefunction will be completely lacking in symmetry.

The symmetry property of the initial trial function may be destroyed by rounding errors in the SCF iteration, but otherwise this property will be carried over to the final HPHF function, and so the above scheme may serve to classify the solutions. It will be seen that the number of solutions which are totally symmetrical (types (I) and (II)), is expected to be equal to the number of non-degenerate IR's of the molecular point-group. A completely unsymmetrical solution of type (IV) is only expected if it has the lowest energy, since otherwise it will converge on one of the other types. Solutions of type (III), which may be said to have partial symmetry, will be expected when the molecular point-group has degenerate IR's.

These arguments allow us to understand the multiple solutions obtained in our calculations. Solutions of type (I), where all orbitals are symmetry orbitals, were found for all molecules, being the ones numbered (2) for H_2O, (3) for CO, and solutions presented for NH_3 and CH_4. Solutions (3) and (4) for H_2O are examples of type (II), where the $\{a\}$ and $\{b\}$ are not symmetry orbitals, although the wavefunction is fully symmetrical. Thus solution (3) was obtained either by mixing the RHF $1b_2$ orbital with the virtual $4a_1$ to form the initial function, or the filled $3a_1$ with the virtual $2b_2$, so that ϕ_2 has the symmetry B_2. In solution (4) the symmetry of ϕ_2 is B_1, and our discussion leads us to expect a third solution of this type, where ϕ_2 has the symmetry A_2. We attempted to find this solution by initial mixing of the $1b_1$ filled orbital with the virtual $2b_2$, but if this solution exists, it appears to have a very shallow energy surface, with a minimum so little below the RHF energy, that the calculation would not converge.

Solutions of type (III) are exemplified by numbers (1) and (2) in Table 3. In the first, obtained by mixing 5σ with the virtual 2π orbital, ϕ_2 has Π symmetry, and in the second, from mixing $1\pi_x$ with $2\pi_y$, ϕ_2 contains some Δ symmetry. In neither of these cases is the wavefunction completely symmetrical about the molecular axis. Solutions of this type are also expected for NH_3 and CH_4, but we failed to find them, possibly because the symmetry of the initial function was destroyed by rounding errors, so that the SCF procedure converged onto the lowest energy solutions.

Our symmetry discussion, although throwing valuable light on the existence of multiple HPHF solutions, and the way in which these are obtained from different starting points, clearly cannot say anything about the relative energy of the solutions, or about their physical significance. Although some of the higher energy solutions do seem to have a certain physical significance – for example number (1) for CO shows most correlation coming from the 5σ lone-pair orbital – it may be argued in general that the physically interesting solution is that with the lowest energy, either with or without symmetry constraint. In all four cases studied here the lowest energy solution in which the wavefunction has the full symmetry of the molecule is of type (I): that is the orbitals are symmetry orbitals. This is understandable if the predominant correlation comes from electrons in the bonds. Thus in AH_n molecules the $\{a\}$ orbitals will have more density on the central atom and the $\{b\}$ orbitals on the hydrogen atoms (or *vice-versa*), and this can be achieved without loosing the symmetry of the orbitals. The same applies to heteronuclear diatomic molecules such as CO, but this will not always be the case: in a homonuclear diatomic the orbitals will loose the centre of symmetry, if the $\{a\}$ and $\{b\}$ sets are concentrated on different atoms. We might then expect a solution of type (II) to be lowest in energy, ϕ_2 having Σ_u symmetry. This is indeed the case for H_2, mentioned in our previous paper [9].

Solutions of type (IV), where the wavefunction is not fully symmetrical, were found for three of the molecules studied here, (H_2O, NH_3, and CO), and for BH, reported in [9]. The nature of these solutions seems to confirm the discussion of our previous paper [9], where it was suggested that the HPHF wavefunction may be quite good at describing correlation in a single pair of electrons, but less good for the simultaneous correlation of several pairs. In all the non-symmetrical solutions obtained, most of the correlation energy comes from a single pair of electrons. Thus in solution (1) for water, only one pair of orbitals differs appreciably between the $\{a\}$ and $\{b\}$ sets, the corresponding orbitals being:

$$a \sim 0.6\ \mathrm{H2}(1s) - 0.6\ \mathrm{O}(2s) + 1.0\ \mathrm{O}(2p_x) + 1.2\ \mathrm{O}(2p_y)$$

$$b \sim 0.2\ \mathrm{H1}(1s) + 1.7\ \mathrm{H2}(1s) - 0.6\ \mathrm{O}(2s) + 0.3\ \mathrm{O}(2p_y).$$

Clearly this pair of orbitals is strongly correlated in the single bond O–H2, and this solution would be the most appropriate one for a potential surface where one O–H bond was being dissociated. A similar solution was found for NH_3, and in solution (4) for CO, it can be seen that much more correlation comes from the $1\pi_x$ than from the $1\pi_y$ orbital. However, the factors which determine whether an unsymmetrical solution will exist must be rather subtle, since for CH_4 the type (I) solution seems to have the lowest energy.

4. Conclusions

The aim of this work was to explore some of the features of the HPHF wavefunction, and of the method of calculation which we described previously. We have found the calculations easy to perform, with no problems of convergence. However, the existence of multiple solutions makes the choice of starting point very important. In simple molecules, physical arguments combined with symmetry considerations should allow the desired solution to be selected from the beginning, but it is by no means certain that this will always be the case with larger molecules.

The correlation energy given by the HPHF method is disappointingly small, and the method clearly cannot compete in this respect with more sophisticated calculations [12–16]. However for certain problems, where the correlation of a single pair of electrons is important, the HPHF function may give a marked improvement over RHF, with only a moderate increase in computation. It may also be possible to find a similar method which is applicable to open-shell molecules and excited states, and this is something which we are at present considering.

P.A. Cox is grateful to the Royal Society for a European Exchange Programme Fellowship, and M.H. Wood for a N.A.T.O. Post-Doctoral Fellowship. We would both like to thank Professor A. Veillard for his hospitality at the Institut de Chimie in Strasbourg.

References

1. Slater,J.C.: Rev. Mod. Phys. **6**, 209 (1934); Phys. Rev. **81**, 385 (1951)
2. Amos,A.T., Hall,G.G.: Proc. Roy. Soc. **A263**, 483 (1961)
3. Löwdin,P.O.: Phys. Rev. **97**, 1509 (1955)
4. Bunge,C.: Phys. Rev. **154**, 70 (1967); Lunell,S.: Phys. Rev. **173**, 85 (1968)
5. Lefebre,R., Smeyers,Y.G.: Intern. J. Quantum. Chem. **1**, 403 (1967)
6. Grein,F., Chang,T.C.: Chem. Phys. Letters **12**, 44 (1971)
7. Burden,F.R.: Intern. J. Quantum. Chem. **6**, 647 (1972)
8. Smeyers,Y.G., Doreste-Suarez,L.: Intern J. Quantum Chem. 7, 687 (1973)
9. Cox,P.A., Wood,M.H.: Theoret. Chim. Acta (Berl.), **41**, 269–278 (1976)
10. Hehre,W.J., Stewart,R.F., Pople,J.A.: J. Chem. Phys. **51**, 2657 (1969)
11. Schaeffer III,H.F., Bender,C.F.: J. Chem. Phys. **55**, 1720 (1971)
12. Robb,M.A., Csizmadia,I.G.: Intern. J. Quantum. Chem. **4**, 365 (1970)
13. Wood,M.H., Veillard,A.: Mol. Phys. **26**, 595 (1973)
14. Meyer,W.: J. Chem. Phys. **58**, 1017 (1973)
15. Roos,B.: Chem. Phys. Letters **15**, 153 (1972)
16. Bender,C.F., Davidson,E.R.: J. Phys. Chem. **70**, 2675 (1966)

Dr. M.H. Wood
Theoretical Physics Division
AERE Harwell
Oxfordshire, England