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# Unrestricted Hartree–Fock Functions for the Carbon and Fluorine Atoms

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An attempt to solve the Hartree–Fock equations for the (non-relativistic) carbon and fluorine atoms is reported. No constraints are placed on the minimisation of the parametrised energy function arising from the use of the finite expansion method within the single determinant model of atomic electronic structure except those implicit in the expansion method itself.

**Key words:** Hartree–Fock – Carbon – Fluorine.

## 1. Introduction

The use of atomic or molecular symmetry to classify the solutions of the Hartree–Fock equations and so to factorise these equations dates from the very beginning of the Hartree–Fock model both in its numerical [1] and finite expansion [2] forms. Unfortunately this extremely attractive and computationally convenient method is without a theoretical basis. In fact, in a relatively recent proof of the existence of the solutions of the HF equations for neutral systems, Lieb and Simon [3] were unable to find any justification for the idea that individual atomic or molecular orbitals should be related to the symmetry of the one-electron part of the effective Hamiltonian. In fact, it is easy to see that the imposition of these atomic or molecular "symmetries" does constrain the single-determinant wave function to exclude physical effects which are normally thought to be within the HF model. For example, the HF method is usually considered to include the relative polarisations of orbitals (an "average repulsion effect") but the rigid separation of *s*, *p* and *d*... shells specifically excludes the possibility of an unfilled *p* shell polarising an *s*-shell.

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In the case of atoms there are (at least) three distinguishable types of symmetry restriction usually placed on the approximate Hartree–Fock orbitals.

(i) The total wave function is constrained to be a "spin" eigenfunction and/or the individual orbitals are constrained to be eigenfunctions of $\hat{s}^2$ and $\hat{s}_z$.
(ii) The total wavefunction is constrained to be an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ and/or the individual orbitals are chosen to be eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$.
(iii) The "equivalence restriction": sets of orbitals of the same value of $\hat{l}^2$ are constrained to have the same radial function.

These constraints can be combined in various ways and, individually or in conjunction, all conspire to frustrate the action of the variational method leading to (e.g.) saddle points in the energy functional not true minima.

In this note we report the results of carrying through as full a solution as is technically possible of the unconstrained HF equations for two atoms using the finite expansion method. In this approach the HF energy functional is replaced by a parametrised energy function: we term this approach the "parametrised variation method".

## 2. The Carbon and Fluorine Atoms – approximate Hartree–Fock Orbitals

The carbon and fluorine atoms were chosen since they are the most clear-cut cases where the negative atomic ions are predicted by the constrained HF model to be stable and we wish to take up the problem of the existence of HF orbitals for negative ions elsewhere.

Clementi's tables [4] give the following energies (in atomic units) for the carbon and fluorine atoms

| C | F |
|---|---|
| −37.688611 | −99.409284 |

These results are obtained by a combined linear/non-linear optimisation of a set of STOs within the spherical approximation, the equivalence restriction and the "spin" eigenfunction constraint.

We have carried through the unconstrained solution of the parametric variation method for the two atoms. The basis functions were STOs and, because of the rather heavy computational burden involved in the optimisation of the non-linear parameters (orbital exponents), we adopted a device which will render our non-linear optimisations not quite complete. We added "symmetry-breaking" basis functions to a double-zeta basis, optimised the exponents of the new orbitals and then did the final calculation with Clementi's "Hartree–Fock basis" in place of the double-zeta basis. It is clear that the optimum "symmetry-breaking" basis functions would differ slightly between the two "symmetry-adapted" bases but there are good reasons to suspect that the differences would be very small. In any case, to optimise the non-linear parameters for a large basis of *s*, *p*, *d*, *f*, *g* etc. STOs would quickly exhaust our computer budget.

The basis of STOs was "doubled" by allowing each spatial function to be multiplied by the two "spin" functions and all coefficients were allowed to be complex. In fact, as is known in a variety of contexts, the linear-expansion SCF procedure does tend to "encourage" the retention of spurious symmetries and so at least the initial explanatory runs were done *interactively* on the computing system and the density matrices were changed by small amounts from time to time to encourage the loss of the various symmetries. Thus any one Hartree–Fock orbital can be a linear combination of $s, p, d, f, g \ldots$ with both "spin" components: each orbital may not be an eigenfunction of $\hat{S}_z$, $\hat{l}^2$ or $\hat{l}_z$. One complication which caused some problems with the computer implementation was the necessity of computing a large number of unfamiliar atomic electron repulsion integrals – integrals which, although non-zero, do not appear in the spherical approximation because of the restricted form of the $P$ matrix.

An attempt was made to, as far as possible, separate the effects of the relaxation of the three constraints. The easiest is the "spin" constraint: simply performing a DODS calculation with the existing Clementi basis with the spherical approximation and equivalence restriction gives some measure of this effect. Maintaining the spherical approximation, we can allow the three $p$ orbitals to be different by allowing the corresponding basis functions to have different exponents during the optimisation. Finally, the effect of inter-shell polarisation can be allowed for by adding "polarisation functions" – basis functions of higher $l$ and $m$ values: for a first row atom: $d, f, g$ etc. Naturally these effects are not simply independent and additive; the addition of polarisation functions enables the DODS calculation to have more freedom etc. But we can get an indication of the order of magnitude of the energy terms involved.

The energy results of the various calculations are presented in Tables 1–4. Tables 1 and 2 give the total electronic energies for the various calculations on carbon and fluorine respectively. Tables 2 and 3 give the orbital energies for the "final" augmented "Clementi HF" basis together with some projected experimental

**Table 1.** The Carbon Atom: augmented "Hartree–Fock" basis functions

| Basis | | New STO exponents | Total energy | Comments |
|---|---|---|---|---|
| Clementi[a] | (1) | — | −37.688611 | "RHF" |
| Clementi[a] | (2) | — | −37.689976 | DODS |
| Clementi[b] plus $2 \times 3d_0$ | (3) | 1.8544, 1.0824 | −37.693671 | Polarisation of "$s$" shells |
| As above[b] plus $4f_{-1}, 4f_0, 4f_1$ | (4) | 1.2140 | −37.693679 | Back polarisation of "$p$" shell |
| As above[b] plus $5g_0$ | (5) | 2.0[b] | −37.693680 | Further polarisation of "$s$" shells |

[a] Ref. [5].

[b] Not optimised, energy gradients too low.

**Table 2.** The Fluorine Atom: augmented "Hartree–Fock" basis functions

| Basis | | New STO exponents | Total energy | Comments |
|---|---|---|---|---|
| Clementi[a] | (1) | — | −99.409284 | RHF |
| As above | (2) | — | −99.410900 | DODS |
| As above[b] 2 × $3d_0$ | (3) | 1.9392, 3.2297 | −99.411772 | Polarisation of "$s$" shells |
| As above[b]<br>$4f_{-1}$, $4f_0$, $4f_1$ | (4) | 3.3775 | −99.412126<br>(13) | Back polarisation of "$p$" shells |
| As above[b]<br>$5g_0$ | (5) | 4.0[b] | −99.412126<br>(14) | Almost negligible further polarisation of "$s$" shells |

[a] Ref. [5].

[b] Not optimised, energy gradients too small.

**Table 3.** The Carbon Atom: orbital energies

| Orbital | (1)[a] | (2) | (3) | (4) | (5) | "Expt."[b] |
|---|---|---|---|---|---|---|
| $1s$ | −11.32552 | −11.34553 | −11.34553 | −11.34554 | −11.34554 | −10.8 |
| $1s'$ | −11.32552 | −11.30057 | −11.30057 | −11.30057 | −11.30057 | −10.8 |
| $2s$ | −0.70563 | −0.82916 | −0.82916 | −0.82917 | −0.82917 | −0.715 |
| $2s'$ | −0.70563 | −0.58349 | −0.58349 | −0.58350 | −0.58350 | −0.715 |
| $2p$ | −0.43334 | −0.43907 | −0.43907 | −0.43908 | −0.43908 (5) | −0.395 |
| $2p'$ | −0.43334 | −0.43907 | −0.43907 | −0.43908 | −0.43908 (5) | −0.395 |

[a] See Table 1 for basis.

[b] Ref. [4] p 206.

**Table 4.** The Fluorine Atom: orbital energies

| | Orbital basis[a] | | | | | |
|---|---|---|---|---|---|---|
| Orbital | (1)[a] | (2) | (3) | (4) | (5) | "Expt."[b] |
| $1s$ | −26.38294 | −26.407371 | −26.407257 | −26.407218 | −26.407218 | −25.6 |
| $1s'$ | −26.38294 | −26.359112 | −26.359046 | −26.359022 | −26.359022 | −25.6 |
| $2s$ | −1.57255 | −1.671676 | −1.671906 | −1.671868 | −1.671868 | −1.475 |
| $2s'$ | −1.57255 | −1.474458 | −1.474994 | −1.475017 | −1.475017 | −1.475 |
| $2p_1$ | −0.73001 | −0.786737 | −0.788484 | −0.788658 | −0.788658 | −0.685 |
| $2p_2$ | −0.73001 | −0.786737 | −0.788484 | −0.788658 | −0.788658 | −0.685 |
| $2p_3$ | −0.73001 | −0.735701 | −0.731842 | −0.731690 | −0.731690 | −0.685 |
| $2p_4$ | −0.73001 | −0.674582 | −0.678388 | −0.679899 | −0.679899 | −0.685 |
| $2p_5$ | −0.73001 | −0.673405 | −0.671404 | −0.670603 | −0.670603 | −0.685 |

[a] See Table 2 for basis.

[b] Ref. [4] p 206.

ionisation potentials [5]. There are some very obvious points to be made: first, the "spin" eigenfunction constraint is important in both carbon and fluorine, the DODS calculation showing a significant energy lowering (0.0014 $h$ for C, 0.0016 $h$ for F); secondly there is a law of diminishing returns for the energy lowering as orbitals of higher and higher $l$ value are included in the basis. In the case of the carbon atom there is a relatively large energy lowering on admission of the two $3d_0$ STOs – almost three times the DODS lowering – while, for fluorine the lowering is much less – less, in fact, than the DODS effect. Addition of $4f$ and $5g$ STOs gives very small energy improvements. Indeed, after addition of $5g$ STOs it is rather difficult to optimise the non-linear (orbital exponent) parameter since the gradients are so small ($\sim 10^{-7}$). Nevertheless, the expected polarisations *do* occur as the small but non-zero populations of these higher orbitals show. However, in view of comments to be made in the next section, it would prove no surprise to us if our optimisations proved to be incomplete.

## 3. Comments on the Approximate Hartree–Fock Orbitals

The first thing to note is that the spatial orbitals are not eigenfunctions of $\hat{l}^2$: the "$2s$" orbital of carbon consists, for example, of a dominant contribution of $s$ character combined with smaller amounts of basis functions of even $l$: $d$ and $g$ in our approximation. Also the incomplete "$p$" shell means that the DODS part of the solution operates; the "$2s$" and "$1s$" orbitals are different for different "spins". Repeated attempts to force the orbitals of even and odd $l$ to mix – by starting the calculation with non-zero elements in the "mixing" positions – failed as did attempts to get basis functions of different "spin" to form combinations. Also, only the $3d_0$ basis functions mixed with the $s$-type basis functions and only $4f_{-1}$ with $p_{-1}$-type (and $4_{f0}$ with $p_0$, $4f_1$, with $p_1$). The orbitals remaining eigenfunctions of $\hat{l}_z$ in the face of all odds. We thus have some empirical evidence for the symmetries of the atomic Hartree–Fock orbitals. This evidence is naturally not at all conclusive since it is limited by the fact that we have only used basis functions of a very limited type; containing spherical harmonics and exponential radial functions. Notwithstanding the shaky empirical nature of the evidence we may conjecture (for future *theoretical* investigation) that the Hartree–Fock orbitals of atoms may well be eigenfunctions of $\hat{s}_z$, $\hat{l}_z$ and the parity operator. We specifically exclude $\hat{s}^2$ since there is no scope in the "spin"-space for "spin" functions which are not eigenfunctions of $\hat{s}^2$. The individual orbitals are not eigenfunctions of $\hat{l}^2$. The resultant single-determinant wave function is found to be an eigenfunction of the many-electron operators $\hat{S}_z$ and $\hat{L}_z$ but not of $\hat{L}^2$ or $\hat{S}^2$. If we accept, for the moment, the validity of our deductions that the only "conserved" spatial quantities are $\hat{l}_z$ and parity then none of the four co-ordinate systems in which the hydrogen atom Schrodinger equation separates [6] will separate the atomic Hartree–Fock equations. We can therefore see no need to maintain the traditional form of variational trial functions:

$$Y_l^m(\theta, \phi)R(r).$$

The theoretical evidence does not justify it and the empirical numerical evidence is against it. We hope to return to this problem in a later report.

Examination of Table 4 which gives the orbital energies at various levels of approximation shows a departure from the equivalence restriction for fluorine (which does not occur for carbon – but see later). The five occupied "$2p$" AO's do not all have the same orbital energy – in fact there are four different $2p$ orbital energies. This phenomenon occurs even at the DODS level with the usual $s$ and $p$ only basis. This breakdown of the equivalence restriction naturally suggests that we should go back to the original restricted bases used as starting point and allow the $2p$ STOs to have "different exponents for different $m$ values" to attempt to make up for any deficiencies in the restricted STO basis. So, in fact, we attempted to "re-optimise" the double-zeta basis of Clementi by freeing the six $2p$ STO exponents completely. Several calculations were tried using the original restricted STO basis and bases for which slight changes were made among a given set of three to "encourage" any splitting.

In fact it was found that the double zeta basis functions for the fluorine atom, when given complete freedom *did* become different for different $m$ values, in marked contrast to those of the carbon atom which resisted attempts to make them split. Naturally, having re-optimised the starting basis, the two $3d_0$ functions were re-optimised but found to be little changed. However the total energy was lowered as in Table 5.

The only real qualitative change on admitting different exponents for different $2p$ STOs was the complete disappearance of any trace of the equivalence restriction. Using the basis of Table 5 the Hartree–Fock calculation for the fluorine atom gives a single determinant of 9 orbitals each of which is different; i.e. all nine have different orbital energies.

**Table 5.** The Fluorine Atom: re-optimisation of the "double-zeta" $2p$ STOs plus addition of higher $l$-value STOs (as Table 2)

| | Description of orbital basis | | | |
|---|---|---|---|---|
| Orbital | $C\,\&\,R^a$ (RHF) | $C\,\&\,R^a$ (DODS) | Double zeta[b] | Double zeta + higher $l$ |
| $1s$ | −26.37355 | −26.396318 | −26.400378 | −26.400496 |
| $1s'$ | −26.37355 | −26.350034 | −26.353528 | −26.353749 |
| $2s$ | −1.56652 | −1.659895 | −1.663928 | −1.665433 |
| $2s'$ | −1.56652 | −1.473032 | −1.474423 | −1.476830 |
| $2p_1$ | −0.72392 | −0.773226 | −0.830601 | −0.838391 |
| $2p_2$ | −0.72392 | −0.773226 | −0.726832 | −0.723644 |
| $2p_3$ | −0.72392 | −0.725438 | −0.726692 | −0.723505 |
| $2p_4$ | −0.72392 | −0.674574 | −0.675381 | −0.680340 |
| $2p_5$ | −0.72392 | −0.674295 | −0.675264 | −0.680222 |
| Total energy | −99.401309 | −99.401883 | −99.402779 | −99.407737 |

[a] Roetti, C., Clementi, E.: J. Chem. Phys. **60**, 4725 (1974).

[b] Different $2p$ exponents for different $m$-values (6 independent exponents).

On the general matter of convergence it was found that there was absolutely no difficulty in getting the augmented basis calculations to converge: what was difficult was obtaining convergence to the ground state. The only sure way of obtaining a sequence of augmented bases which converge to the same (assumed) ground state is to make the basis extensions piecemeal and to use the smaller basis density matrices as starting points for the new calculation. If this is not done with some care one often obtains smooth (linear *and* non-linear) convergence to any number of higher "states". Sometimes it is easy to identify the "state" concerned and make a correspondence with the symmetry-restricted calculation (or with experiment); so convergence to the $^1S$ or $^1D$ components of $p^2$ is possible (and likely!). Occasionally, the calculation goes smoothly to an even higher "state" *and*, much more surprisingly in the case of carbon, to a "state" which is (in energy) *between* the $^3P$ and $^1D$ restricted calculations. It seems at least likely that this self-consistent solution of the linear expansion approximation to the HF equations is a turning point of the parametrised energy function but is unlikely to be a turning point of the HF energy functional and is almost certainly not a turning point of the energy functional associated with the true Hamiltonian. In short, it is an artifact of the parametrisation scheme.

The orbital energies quoted in Tables 3 and 4 can be compared to certain experimental ionisation potentials. In the case of carbon there is little change in the highest orbital energy (−0.433 to −0.439; experiment 0.395) and the agreement with experiment is hardly affected. However, for fluorine the change is larger and the agreement with experiment is much improved (−0.730 to −0.671; experiment 0.685). What is more interesting however are the large changes in the lower orbital energies, particularly the large splitting of the 2*s* AOs. It is difficult to compare these numbers with experiment since the conventional analysis of atomic spectral data assumes the restricted form for the atomic wavefunction.

## 4. Limitations

There is one main qualification to be made to all the computed results presented here, namely that all optimisations of non-linear parameters are, in all probability, incomplete. There are two reasons for this. In the first place we have used a double zeta basis as a starting point in adding "symmetry breaking" basis functions and relaxing constraints without too much effort at re-optimising the double-zeta basis. Further, the optimised additional basis functions were simply added to a "symmetry-restricted Hartree–Fock" basis in order to get an estimate of the atomic energies – again no re-optimisation of the original basis was attempted. This leads us on to the second point; the enormous computational cost of performing completely general solutions of the Hartree–Fock equations; even for atoms. For example, in Clementi's reported restricted Hartree–Fock calculations for the fluorine atom a set of six *s* and four *p* STOs are used to expand the orbitals, this means, at most, the diagonalisation of a $6 \times 6$ real symmetric matrix. If the same basis (i.e. without higher angular momentum polarisation functions) is used in a general approach the basis is $(6+4\times 3)\times 2$ i.e. 36 which, together with the use of complex coefficients is roughly equivalent to the diagonalisation of a 72 × 72 real symmetric matrix: an increase of about (72/6) cubed in computation time – a factor of 1728. If now, two $3d$, three $4f$ and one $5g$ functions are added to the basis the factor becomes (96/6) cubed (4096) plus the increased complexity of the higher integrals. Also, the number of non-zero atomic integrals is much larger since the whole set must be included in the absence of any restrictions on the form of the density matrix. Thus the *routine* calculation of atomic Hartree–Fock functions is out of the question.

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