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Commentationes

Non-Empirical LCAO-MO-SCF-CI Calculations on Organic Molecules with Gaussian Type Functions

Part III. Atomic Calculations

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This part of the series presents the results obtained by open shell SCF computations on the C, N, O, and F Atoms.

Dieser Teil der Reihe gibt die Ergebnisse von SCF-Rechnungen für offene Schalen am C, N, O und F an.

Cette partie de la suite d'articles présente les résultats obtenus par des calculs SCF à couches ouvertes sur les atomet C, N, O et F.

In molecular quantum mechanics it is always a problem to choose exponents for the basis functions. This is particularly true in the case of Gaussian type functions (GTF) where no guide, like the Slater rule in the case of exponential type functions (ETF), is available. If the molecule is small [14, 15] the best policy is to use Huzinaga's exponents [8]. For small basis sets however no optimized exponents are available. To overcome this problem the most desirable choice is to optimize the exponents on the molecule which is to be studied. This has been done in the case of HCN [10] and NF_2 positive ion [9], however the computer time

Table 1. *Electronic Energies of* C, N, O and F *Atoms in their lowest Electronic States as calculated with various Gaussian Basis Sets*

	3^s	5^s	7^s	3^s	5^s	7^s
	$C(^3P)$			$N(^4S)$		
1^p	−35.4511	−37.0943	−37.2573	−51.0255	−53.2242	−53.4445
2^p	−35.7322	−37.3899	−37.5573	−49.0841	−53.9110	−52.0862
3^p	−35.7958	−37.4503	−37.6192	−50.9663	−52.9539	−54.2846
HF limit [8, 2]			−37.6886			−54.4009
	$O(^3P)$			$F(^2P)$		
1^p	−69.8588	−72.6955	−72.9861	−92.5402	−95.664	−96.3364
2^p	−71.1392	−74.0429	−74.3431	−94.7335	−98.2695	−98.6516
3^p	−71.4254	−74.3283	−74.6326	−95.2236	−98.7609	−99.1486
HF limit [8, 2]			−74.8094			−99.4093

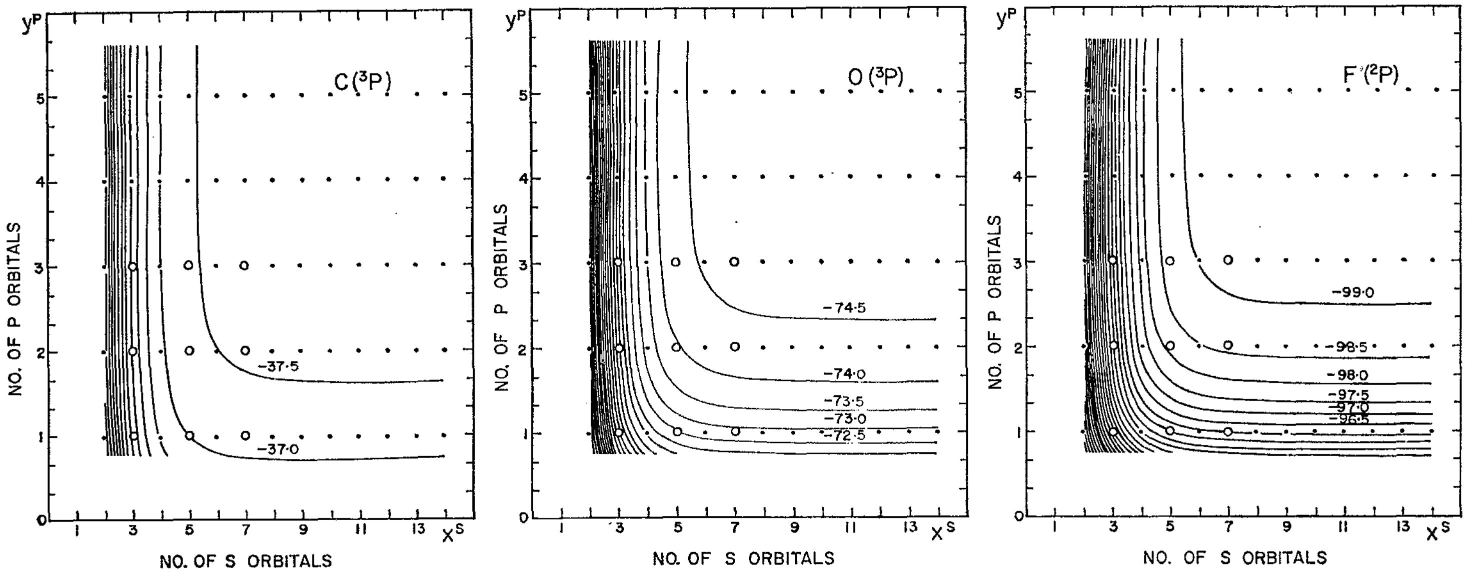

Fig. 1. Energy Surface Contours of C, O, and F atoms as the function of Basis Set Size

Table 2. *Orbital Energies of* C, N, O *and* F *atoms in their lowest Electronic States as calculated with Selected Basis Sets*

Basis Set	Type Size	$3^s + 1^p$ 6	$5^s + 2^p$ 11	$7^s + 3^p$ 16	STO HF[2]
C	1*s*	−10.0514	−10.7238	−10.7543	−11.3255
	2*s*	+ 0.2145	− 0.1842	− 0.2254	− 0.7056
	2*p*	+ 0.0787	− 0.1945	− 0.2466	− 0.4333
N	1*s*	−14.7715	−15.5635	−15.5671	−15.6289
	2*s*	− 0.1031	− 0.5126	− 0.5586	− 0.9452
	2*p*	+ 0.2498	− 0.1185	− 0.1851	− 0.5675
O	1*s*	−19.0416	−19.8422	−19.8365	−20.6686
	2*s*	+ 0.0810	− 0.4990	− 0.5612	− 1.2442
	2*p*	+ 0.4753	− 0.0011	− 0.0999	− 0.6319
F	1*s*	−24.1710	−24.9256	−24.9200	−26.3829
	2*s*	+ 0.1837	− 0.5501	− 0.6317	− 1.5726
	2*p*	+ 0.6994	+ 0.1144	− 0.0221	− 0.7300

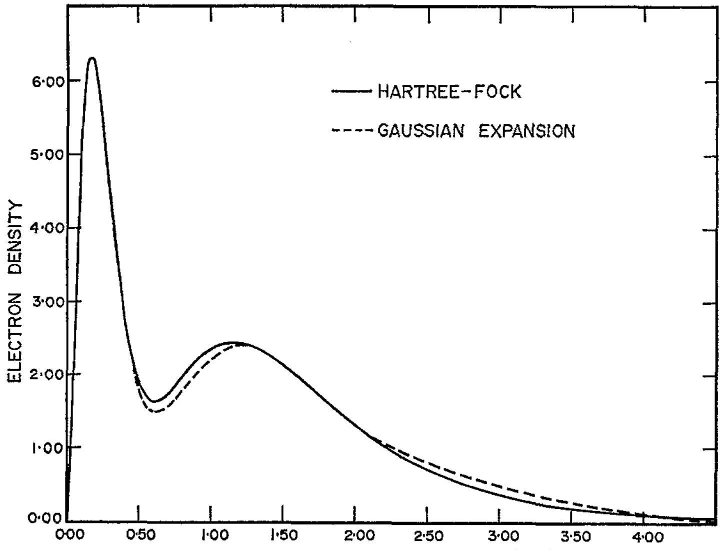

Fig. 2. Radial Electron Density of C-atom as calculated from Hartree-Fock Atomic Orbitals and from Self Consistent Field Atomic Orbitals obtained by the best Gaussian Expansion ($7^s + 3^p$)

requirement is enormous. In a recent attempt optimized exponents of C and O atoms were obtained using minimal GTF basis sets (3^s, 1^p). When these optimized basis functions were used in calculating bond angles and barrier height for CH_3^- and H_2O respectively the results were surprisingly disappointing [16]. Similar computations using scaled exponents [5] gave relatively good results [15, 16]. This indicated that if one needs semiquantitative results the best policy still is to use scaled exponents of GTF as published previously [5] and used extensively [1, 4, 6, 7, 11, 12, 13, 17, 19].

For this reason it seemed desirable to release the results of atomic calculation carried out at MIT in 1963 on the C, O, F atoms and at the University of Toronto in 1966 on the N atom. The computation was carried out within the framework of Roothaan's open shell SCF formalism [18] as discussed before [5] using a modified POLYATOM system [3].

Total energies calculated for C, N, O and F atoms are summarized in Tab. 1 where the Hartree-Fock values are given for comparison. Energy contours for the C, O, and F atoms are shown in Fig. 1. From both Tab. 1 and Fig. 1 it seems obvious that the line of steepest descent is along the diagonal ($3^s + 1^p \rightarrow 5^s + 2^p \rightarrow 7^s + 3^p$). These results are in agreement with the pattern observed in the case of formyl fluoride [6]. Orbital energies are summarized in Tab. 2. The radial electron density of the C-atom for the larger basis set ($7^s + 3^p$) is shown in Fig. 2.

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