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On the Use of Small Atomic Basis Sets in Non-Empirical Molecular Calculations

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The quality of an atomic basis set in molecular calculations can be characterized by the deviation of the valence-shell orbital energies from their values in a Hartree-Fock limit calculation. For atoms of a certain row of the periodic system, this quality appears to depend not only on the number of basis functions used in the calculations, as is usually accepted, but also on the number of valence shell electrons of the various atoms.

As a consequence of this result, rules can be formulated for the combination of small atomic basis sets to a basis set for a molecular calculation. In fact, the best results are obtained with basis sets in which the deviations of all atomic valence shell orbital-energies from their Hartree-Fock limit values are of the same order of magnitude.

Die Qualität eines Atombasissatzes zur Rechnung an Molekülen kann durch die Abweichung der Energien der Orbitale der Valenzschalen von den Werten einer Hartree-Fock-Grenzrechnung charakterisiert werden. Im Falle der Atome einer bestimmten Periode im Periodensystem scheint diese Qualität nicht nur von der Zahl der bei der Rechnung benutzten Basisfunktionen abzuhängen, wie allgemein akzeptiert ist, sondern auch von der Anzahl der Elektronen der Valenzschale der verschiedenen Atome.

Aufgrund dieses Resultats können Regeln zur Kombination kleiner Atombasissätze zu einem Basissatz für Rechnungen an Molekülen formuliert werden. In der Tat werden die besten Resultate mit Basissätzen erhalten, bei denen die Abweichungen aller Orbitalenergien der Atomvalenzschalen von ihrem Hartree-Fock-Grenzwert in der gleichen Größenordnung sind.

Introduction

In general non-empirical molecular calculations are performed with a set of basis function built up from atomic basis sets. The last few years a large number of atomic basis sets have been published, both with Gaussian Type Orbitals (GTO's) [1–6], and with Slater Type Orbitals (STO's) [7–9]. It is dangerous, however, to use just some arbitrary combination of atomic basis sets in a molecular calculation, since there is a possibility that the resulting basis set is "unbalanced" as indicated by Mulliken [10]. Unbalanced basis sets may lead to an incorrect prediction of various quantities like dipole moments or charge distributions obtained from a population analysis.

In molecular calculations, usually little attention is paid to the question which combination of atomic basis sets on the various atoms in the molecule can be used to result in a balanced basis.

Since at this moment a large number of atomic basis sets is available, we want to be able to compare the quality of these basis sets and to decide which basis sets can be combined.

Usually the quality of an optimized atomic basis set is assumed to be determined by the number of functions of the various symmetry types in the set, e.g.

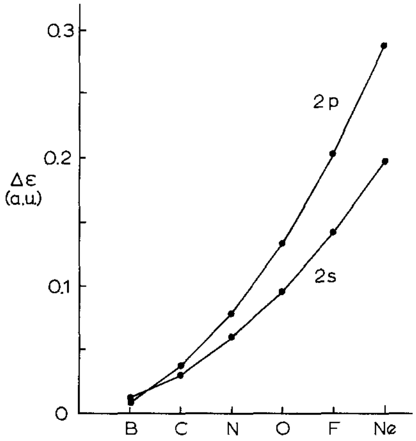

Fig. 1. $\Delta\varepsilon_{2s}$ and $\Delta\varepsilon_{2p}$ obtained with a minimum STO basis for the averaged configuration s^2p^n of the atoms B to Ne

for a certain atom a set consisting of three *s*-type functions and two *p*-type functions, a (3, 2) set, is better than a set consisting of two *s*-type functions and one *p*-type function, a (2, 1) set.

There is, however, another parameter that affects the quality of the basis set. Even when an atomic basis set is completely optimized, the deviations of the orbital energies calculated with this basis set from the values obtained in the Hartree-Fock limit, are a function of the number of electrons in the different shells of the atom. This effect especially shows up when an atomic shell is being filled. For example, in a set of calculations for the first-row atoms with a fixed number of *s*- and *p*-type basis functions the difference between ε_{2p} in these calculations and ε_{2p} in the Hartree-Fock limit,

$$\Delta\varepsilon_{2p} = \varepsilon_{2p}(\text{calc}) - \varepsilon_{2p}(\text{H.F.})\,, \tag{1}$$

becomes rapidly larger going from B to Ne. The value of $\Delta\varepsilon_{2s}$, similarly defined as

$$\Delta\varepsilon_{2s} = \varepsilon_{2s}(\text{calc}) - \varepsilon_{2s}(\text{H.F.})\,, \tag{2}$$

also becomes larger, but less than the value of $\Delta\varepsilon_{2p}$.

As an illustration the values of $\Delta\varepsilon_{2s}$ and $\Delta\varepsilon_{2p}$ for a minimal STO calculation are shown in Fig. 1 for the averaged configurations s^2p^n of the atoms B through Ne. Likewise, the same dependence of the quality of the basis set on the number of electrons can be found for other basis sets, GTO sets and STO sets of any size. However, for larger basis sets the effect rapidly becomes much less pronounced. This effect is not restricted either to atoms with *s*- and *p*-type functions. A similar effect occurs with the *d*-electrons of transition metal atoms.

Theory

If we want to discuss the origin of the deviations of the orbital energies, we first have to analyse the effect somewhat more in detail. The values of $\Delta\varepsilon_i$ for a series of atoms in which one shell is being filled, obtained with basis sets of the same size, may be expanded in a limited power series in n, the number of electrons in that particular shell.

The coefficients of the different powers of n are shown in Table 1 for the $\Delta\varepsilon_{2p}$ values of some STO basis sets for the first row atoms [11]. Terms that do not make a significant contribution to the fit of the expansion are omitted. In this table we see that if the values of $\Delta\varepsilon$ are relatively small, there is a linear correlation between $\Delta\varepsilon$ and n. If, however, the deviations are larger, a quadratic term appears.

In the same way we can analyse the mean deviation of the function calculated in a certain basis from the corresponding function in the Hartree-Fock limit, defined as

$$\langle \Delta\Psi_{2p}\rangle = \left[\int \{\Psi_{2p}(\mathrm{H.F.}) - \Psi_{2p}(\mathrm{calc})\}^2 \, d\tau\right]^{\frac{1}{2}} \tag{3}$$

for the same STO-basis sets. The results of these calculations are shown in Table 2. From these results we may conclude that the linear dependance of $\langle \Delta\Psi\rangle$ of n is small compared with the constant term. We therefore may introduce as a perturbation in our Hartree-Fock equations some $\Delta\Psi$ that is independent of n.

Suppose we want to solve the Hartree-Fock equations

$$F(1)\,\Psi_i(1) = \varepsilon_i\,\Psi_i(1) \tag{4}$$

by expanding Ψ_i in a limited basis set. The resulting solution $\tilde{\Psi}_i$ in general will deviate from the correct solution Ψ_i (Hartree-Fock limit). This in turn affects the Hartree-Fock operator F, defined by

$$F(1) = h(1) + \sum_k \int \Psi_k(2)\,\frac{(1-P_{12})}{r_{12}}\,\Psi_k(2)\,d\tau_2 \tag{5}$$

yielding

$$\tilde{F}(1) = h(1) + \sum_k \int \tilde{\Psi}_k(2)\,\frac{(1-P_{12})}{r_{12}}\,\tilde{\Psi}_k(2)\,d\tau_2\,. \tag{6}$$

Introducing $\Delta\Psi_i = \tilde{\Psi}_i - \Psi_i$ the deviation in the Hartree-Fock operator will be

$$\Delta F(1) = \sum_k \int \Delta\Psi_k(2)\,\frac{(1-P_{12})}{r_{12}}\,\Psi_k(2)\,d\tau_2 + \sum_k \int \Psi_k(2)\,\frac{(1-P_{12})}{r_{12}}\,\Delta\Psi_k(2)\,d\tau_2\,. \tag{7}$$

We now can calculate the deviation in the one-electron energies according to

$$\Delta\varepsilon_i = 2\langle \Delta\Psi_i | F | \Psi_i\rangle + \langle \Psi_i | \Delta F | \Psi_i\rangle\,. \tag{8}$$

The result is

$$\begin{aligned}\Delta\varepsilon_i = 2\langle \Delta\Psi_i | h | \Psi_i\rangle &+ 2\sum_k \left[(\Delta\Psi_i\Psi_i | \Psi_k\Psi_k)\right.\\ &\left.- (\Delta\Psi_i\Psi_k | \Psi_i\Psi_k) + (\Psi_i\Psi_i | \Delta\Psi_k\Psi_k) - (\Psi_i\Delta\Psi_k | \Psi_i\Psi_k)\right].\end{aligned} \tag{9}$$

The summation over k in the Eqs. (5) to (9) is in principle over all electrons. This summation can be seperated into a summation over electrons in inner shells and a summation over electrons in the valence shell. The first sum contributes to the constant term in Table 1, the second sum leads to a term that is proportional to the number of electrons in the valence shell (since in that case all integrals $\langle \Delta\Psi_i\Psi_i | \Psi_k\Psi_k\rangle$ etc. will approximately have the same value). As a consequence of this, $\Delta\varepsilon_i$ will to a first-order approximation be proportional to n.

Table 1. Coefficients in the power series expansion of $\Delta\varepsilon_{2p}$ in n for a number of STO basis sets for the first row atoms [11]. $10^5\,\Delta\varepsilon_{2p} = a + bn + cn^2 + \cdots$ (non-significant entries are omitted)

	a	b	c
minimal (2, 1)	−316	547	718
marginal (3, 2)	114	170	20
nominal (4, 3)	− 29	15	—

If the deviations in the molecular orbitals are small, we only have to take into account these first-order terms. However, when the deviations are larger, we also have to consider higher-order terms, as can be seen in Table 1 for the minimal basis set.

Atomic Calculations

In Figs. 2 through 5 some examples are given of the change of $\Delta\varepsilon$ with the number of electrons in the open shell. In these examples calculations from literature are used on a special state of a configuration (in general the ground state). Therefore the electronic interaction does not change as smoothly along a series of atoms as for the averaged configuration. Especially nitrogen (^{4}S) and manganese

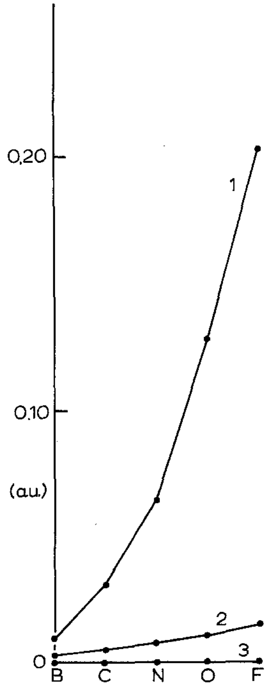

Fig. 2. $\Delta\varepsilon_{2p}$ for a series of STO basis sets. For each line the number of p-type functions is indicated

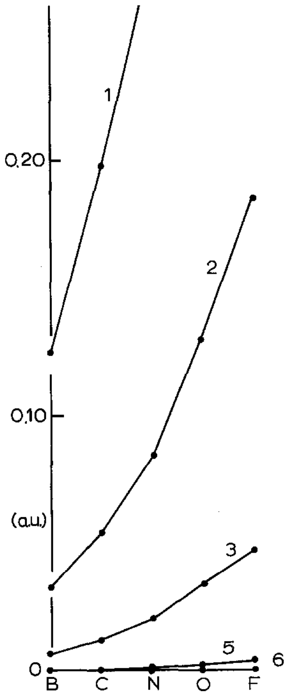

Fig. 3. $\Delta\varepsilon_{2p}$ for a series of GTO basis sets. For each line the number of p-type functions is indicated

(^{6}S), with one electron in each orbital of the open shell, have large exchange contributions that cancel part of the Coulombic repulsion terms and therefore the values of $\Delta\varepsilon$ for these atoms are relatively small.

Fig. 2 shows the values of $\Delta\varepsilon_{2p}$ for a series of STO basis sets with an increasing number of p-type functions and a comparable number of s-type functions [11]. In Fig. 3 the same is done for a series of GTO basis sets [12]. Figs. 4 and 5 illustrate the situation for transition metals. Here, too, all calculations are for the lowest state of the $(3d)^n(4s)^2$ configuration. As reference calculations we used the large basis STO calculations of Clementi [8]. In Fig. 4 the results are given for the calculations of Roos *et al.* [4], who used a basis of nine s-type, five p-type and three d-type GTO's. In Fig. 5 similar results are shown for the basis sets published by Wachters [5], who used a (14, 9, 5) set.

We obtain another illustration, when we consider Van Duyneveldt's [6] large series of optimized atomic GTO basis sets. We can calculate the $\Delta\varepsilon$-values for all calculations of this series, a selection of which is given in Table 3. From this table we see for example that the $\Delta\varepsilon$-values of a boron (5, 3) set are almost equal to the $\Delta\varepsilon$-values of a fluorine (7, 4) set.

All the basis sets discussed so far in this chapter are not contracted. With contracted basis sets the atomic orbitals are disturbed by the contraction and are no longer fully optimized. Now the general trend will be the same, but the position of the curve is contraction-dependent. As an example Table 4 gives $\Delta\varepsilon$-values for the contracted GTO basis sets of Basch *et al.* [13], (15 s-type, 8 p-type and 5 d-

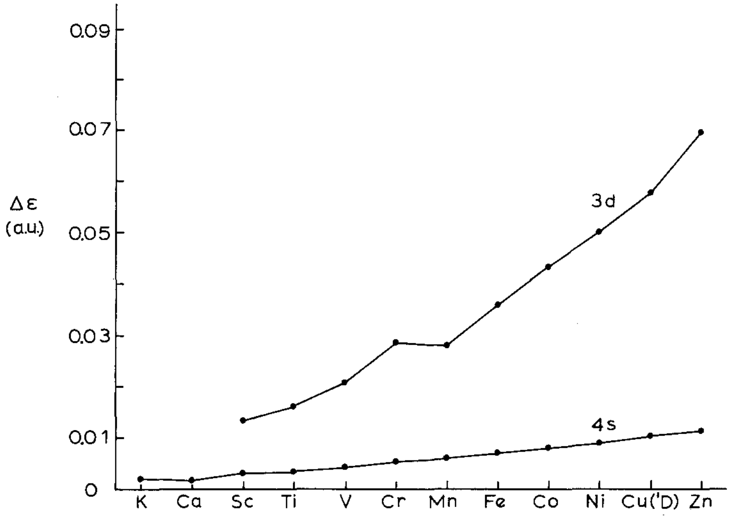

Fig. 4. $\Delta\varepsilon_{3d}$ and $\Delta\varepsilon_{4s}$ for the basis sets of Roos *et al.* [4]

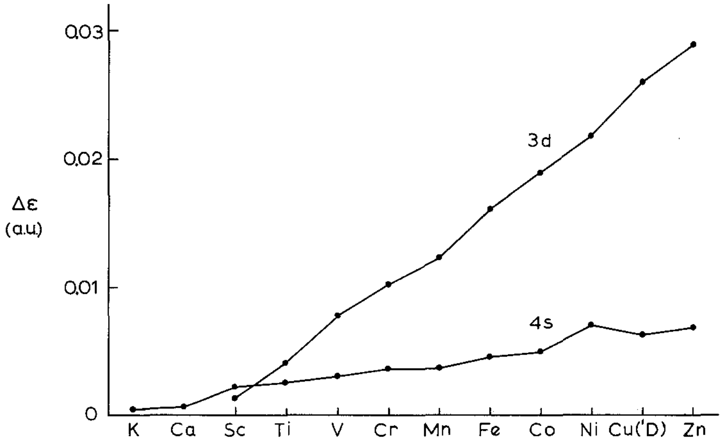

Fig. 5. $\Delta\varepsilon_{3d}$ and $\Delta\varepsilon_{4s}$ for the basis sets of Wachters [5]

Table 2. Coefficients in the power series expansion of $\langle \Delta \Psi_{2p} \rangle$ in n for a number of STO basis sets for the first row atoms. $10^3 \langle \Delta \Psi_{2p} \rangle = a + bn + \cdots$ (non-significant entries are omitted)

	a	b
minimal (2, 1)	97	14
marginal (3, 2)	14	2
nominal (4, 3)	0.01	—

Table 3. E, ε_{1s}, ε_{2s} and ε_{2p} for B to Ne with large accurate basis ΔE, $\Delta\varepsilon_{1s}$, $\Delta\varepsilon_{2s}$ and $\Delta\varepsilon_{2p}$ for a number of basis sets from van Duyneveldt [6]

		B	C	N	O	F	Ne
Large accurate basis	E	-24.529	-37.689	-54.401	-74.809	-99.409	-128.547
	ε_{1s}	-7.695	-11.326	-15.629	-20.669	-26.383	-32.773
	ε_{2s}	-0.495	-0.706	-0.945	-1.244	-1.573	-1.930
	ε_{2p}	-0.310	-0.433	-0.568	-0.632	-0.730	-0.850
(4, 2)	$10^3\Delta E$	193	333	583	834	1228	1731
	$10^3\Delta\varepsilon_{1s}$	63	80	101	124	153	186
	$10^3\Delta\varepsilon_{2s}$	17	29	47	72	102	138
	$10^3\Delta\varepsilon_{2p}$	53	59	89	135	188	249
(5, 2)	$10^3\Delta E$	82	173	321	551	869	1288
	$10^3\Delta\varepsilon_{1s}$	5	-3	-11	-19	-28	-36
	$10^3\Delta\varepsilon_{2s}$	16	28	12	69	99	133
	$10^3\Delta\varepsilon_{2p}$	34	57	75	132	185	244
(5, 3)	$10^3\Delta E$	63	107	170	256	368	508
	$10^3\Delta\varepsilon_{1s}$	18	25	34	45	59	75
	$10^3\Delta\varepsilon_{2s}$	17	28	42	61	84	109
	$10^3\Delta\varepsilon_{sp}$	15	23	33	48	66	85
(6, 3)	$10^3\Delta E$	38	66	106	167	248	353
	$10^3\Delta\varepsilon_{1s}$	16	21	28	37	45	61
	$10^3\Delta\varepsilon_{2s}$	2	5	9	15	23	33
	$10^3\Delta\varepsilon_{2p}$	7	13	20	33	48	65
(7, 4)	$10^3\Delta E$	10	17	28	43	63	89
	$10^3\Delta\varepsilon_{1s}$	4	7	9	13	17	23
	$10^3\Delta\varepsilon_{2s}$	2	2	4	6	3	13
	$10^3\Delta\varepsilon_{2p}$	1	4	6	10	14	19
(8, 4)	$10^3\Delta E$	4	9	16	28	44	65
	$10^3\Delta\varepsilon_{1s}$	1	2	3	5	8	10
	$10^3\Delta\varepsilon_{2s}$	1	2	3	6	9	12
	$10^3\Delta\varepsilon_{2p}$	2	3	5	9	14	19
(9, 5)	$10^3\Delta E$	2	3	5	8	13	19
	$10^3\Delta\varepsilon_{1s}$	1	1	2	2	3	5
	$10^3\Delta\varepsilon_{2s}$	1	1	2	3	3	5
	$10^3\Delta\varepsilon_{2p}$	1	1	2	3	4	6

Table 4. ΔE, $\Delta\varepsilon_{3p}$, $\Delta\varepsilon_{3d}$ and $\Delta\varepsilon_{4s}$ for the contracted GTO basis sets of Basch *et al.* [13]

	ΔE	$\Delta\varepsilon_{3p}$	$\Delta\varepsilon_{3d}$	$\Delta\varepsilon_{4s}$
Sc	0.8203	-0.0115	-0.0121	0.0023
Ti	0.9165	-0.0055	-0.0067	0.0032
V	1.0204	-0.0029	-0.0055	0.0042
Cr	1.1244	-0.0024	-0.0060	0.0047
Mn	1.2462	0.0181	0.0077	0.0062
Fe	1.3573	-0.0042	0.0158	0.0048
Co	1.4881	0.0064	0.0037	0.0058
Ni	1.6419	0.0481	0.0371	0.0090
Cu	1.7882	0.0044	0.0049	0.0075

type GTO's, contracted to 4 *s*-type, 2 *p*-type and 1 *d*-type function, i.e. a (15, 8, 5) set contracted to [4, 2, 1]). The data in this table show that the contraction may result in additional deviations, as can be seen in the case of nickel, where the $\Delta\varepsilon$-values are much larger than for the other atoms. Furthermore the $3p$ and $3d$ orbital energies for Sc through Cr are about 0.005 a.u. below Clementi's values [8], although the total energy is about 1 a.u. above the value from Clementi's calculation. Mostly this effect arises from the frozen core orbitals. Furthermore the incorrect description of the inner orbitals may cause a deformation of the outer orbitals, but this will not be the case when the contracted combinations are carefully chosen as is discussed by Dunning [14].

Molecular Calculations

The results of the previous section show that the deviation in the orbital energies from the Hartree-Fock limit situation depends both upon the number of basis functions and the number of electrons within a shell. This may have its consequences for molecular calculations. It was shown that for a balanced calculation the number of basis functions on different atoms may have to be different, especially when a small basis set is used, as is the case e.g. in calculations on large molecules.

To study the influence in molecular calculations we have performed a set of calculations on the BF molecule using GTO basis sets of different size. We have compared these results with a calculation in which the large basis set of Huzinaga and Arnau [15] was used. This basis set can be characterized as (11, 6) contracted to a [4, 2] set for each of the atoms B and F. In this reference calculation we have deliberately not used polarization functions (*d*-type orbitals and higher), because we wanted to keep the calculations with small and large basis sets comparable. The reference calculation can be considered to approach the *s*, *p*-limit. The basis sets we used in this test are those of Whitman and Hornback [12]. Their quality in atomic calculations is shown in Table 5, which gives the energy differences between the atomic limited basis set calculations and the Hartree-Fock calculation.

Since not all the basis sets that we derive from the results of Whitman and Hornback are optimized, the separate values of $\Delta\varepsilon$ given in Table 5 are not very reliable as a test for the quality of the basis set, since in these cases one or more ε-values may by accident be quite correct, *e.g.* a poor description of the $1s$ orbital may result in an incorrect ε_{1s} but an almost correct ε_{2s}. As a matter of fact, the

Table 5. B and F atomic basis sets. Values of ΔE, $\Delta\varepsilon_{1s}$, $\Delta\varepsilon_{2s}$ and $\Delta\varepsilon_{2p}$ for a number of basis sets from Whitman and Hornback [12]

Basis	B				F			
set	ΔE	$\Delta\varepsilon_{1s}$	$\Delta\varepsilon_{2s}$	$\Delta\varepsilon_{2p}$	ΔE	$\Delta\varepsilon_{1s}$	$\Delta\varepsilon_{2s}$	$\Delta\varepsilon_{2p}$
(3, 1)	0.816	0.253	0.004	0.125	5.267	0.275	0.004	0.595
(3, 2)	0.735	0.351	0.030	0.045	2.992	1.073	0.156	0.218
(3, 3)	0.718	0.359	0.029	0.027	2.495	1.143	0.135	0.094
(4, 2)	0.193	0.071	0.018	0.038	1.230	0.189	0.110	0.201
(4, 3)	0.175	0.081	0.018	0.021	0.731	0.268	0.092	0.080

Table 6. Experimental dipole moment of BF and computed values of the dipole moment from calculations with various basis set. The dipole moments are given in Debye and have a positive sign for (B^-F^+)

Basis	μ_{BF}
Huzinaga	0.51
B(3, 1) F(3, 1)	4.41
B(3, 1) F(3, 2)	0.93
B(3, 2) F(3, 2)	1.59
B(3, 2) F(3, 3)	0.53
B(3, 2) F(4, 2)	1.48
B(3, 2) F(4, 3)	0.43
Experimental [22]	0.5 ± 0.2

combination of ΔE, $\Delta\varepsilon_{1s}$, $\Delta\varepsilon_{2s}$ and $\Delta\varepsilon_{2p}$ gives a more reliable picture. The influence of further optimalization on molecular calculations, however, is small.

The quality of these molecular calculations can be investigated by comparing the calculated dipolemoments with the experimental value [22] or by analysing the wave function using standard methods, like a Mulliken population analysis [16] and density difference maps, in which the difference in electron density along a line or in a plane in the molecule is visualized [17–21].

The calculated dipole moments, given in Table 6, indicate, that the charge distribution found in the calculation with the basis of Huzinaga and Arnau is correct, but that especially in calculations with small basis sets large deformations of the charge distribution may occur.

Table 7. Gross atomic populations and overlap populations in BF from calculations with various basis sets

Basis	Symmetry	N_B	N_F	p_{BF}
Huzinaga	σ	4.24	5.76	0.025
	π	0.13	1.87	0.153
	total	4.50	9.50	0.331
B(3, 1) F(3, 1)	σ	4.40	5.60	0.162
	π	0.52	1.48	0.271
	total	5.44	8.56	0.704
B(3, 1) F(3, 2)	σ	4.34	5.66	0.285
	π	0.25	1.75	0.211
	total	4.84	9.16	0.707
B(3, 2) F(3, 2)	σ	4.45	5.55	0.435
	π	0.24	1.76	0.197
	total	4.93	9.07	0.829
B(3, 2) F(3, 3)	σ	4.45	5.55	0.387
	π	0.15	1.85	0.163
	total	4.75	9.25	0.713
B(3, 2) F(4, 2)	σ	4.40	5.60	0.388
	π	0.24	1.76	0.195
	total	4.88	9.12	0.778
B(3, 2) F(4, 3)	σ	4.40	5.60	0.342
	π	0.15	1.85	0.162
	total	4.70	9.30	0.666

Table 8. Net population per set of orbitals in BF from calculations with various basis sets

Basis	s(B)	$p\sigma$(B)	$p\pi$(B) (each)	s(F)	$p\sigma$(F)	$p\pi$(F) (each)
Huzinaga	3.82	0.41	0.05	3.98	1.77	1.79
B(3, 1) F(3, 1)	3.86	0.46	0.38	3.94	1.58	1.35
B(3, 1) F(3, 2)	3.85	0.35	0.14	3.67	1.85	1.65
B(3, 2) F(3, 2)	3.78	0.45	0.28	3.66	1.68	1.66
B(3, 2) F(3, 3)	3.82	0.43	0.07	3.58	1.66	1.77
B(3, 2) F(4, 2)	3.78	0.43	0.14	3.73	1.67	1.67
B(3, 2) F(4, 3)	3.83	0.40	0.07	3.66	1.77	1.77

A more directly calculated charge distribution is given in Table 7, in which the results of a population analysis for the various computations are shown.

The charge density shift from B to F of 0.5 electron in the calculation using Huzinaga's basis set is rather large in comparison with the experimental dipole moment but this has to be ascribed to the division of the overlap population in two equal parts in a Mulliken population analysis.

In Table 8 the net populations are shown for sets of orbitals of the same type, e.g. the set of the s-orbitals on B. In this table it is especially interesting to see how the p_σ and the p_π populations on F increase and the s population decreases when the basis on this atom, or on both atoms, becomes larger. For larger basis sets these values approach the values from the calculation with the large set from Huzinaga, but using a small number of p-functions on F, the electrons shift to other, energetically more favourable orbitals.

In the electron density difference map, shown in Fig. 6 for the difference between the small basis (B(3, 1) and F(3, 1)) and the large basis calculation, this

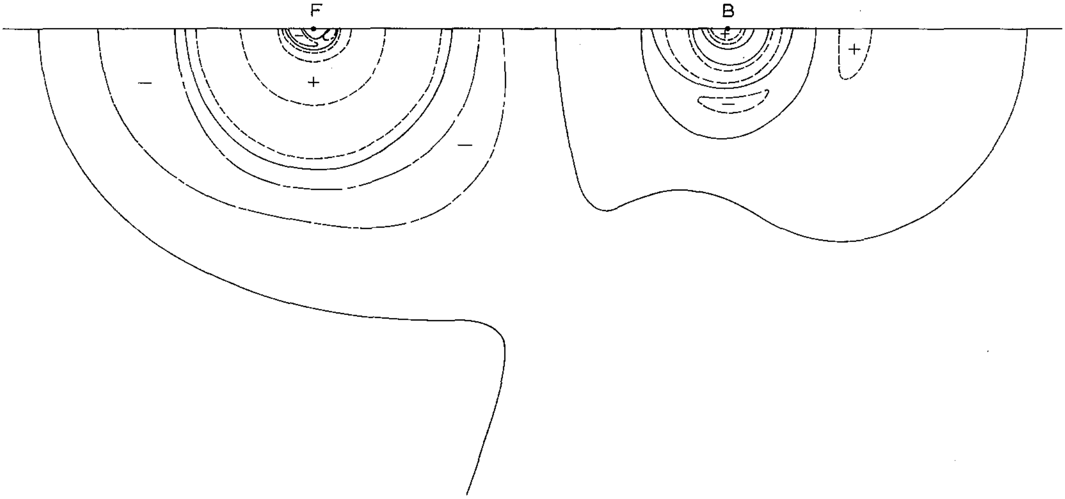

Fig. 6. Density difference map for BF between the small and the large basis calculation. ——— lines of zero density difference, – — – lines of positive density difference, - - - - - lines of negative density difference. Starting from the zero lines, the positive and negative lines represent successively ±0.003, ±0.01, ±0.03, ±0.1

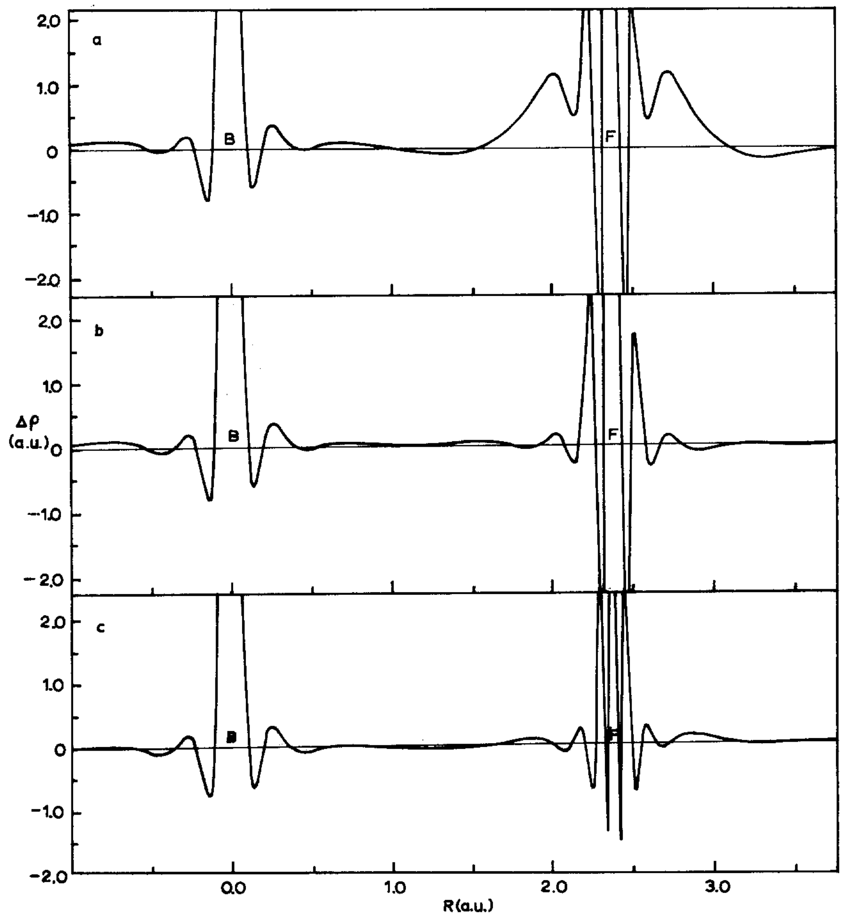

Fig. 7. Density difference along the molecular axis of BF between a number of small-basis calculations and the large-basis calculation. (a) B(3, 1) F(3, 1), (b) B(3, 1) F(3, 2), (c) B(3, 2) F(4, 3)

same effect of a shift from the F $2p$ orbitals to other orbitals shows up. The effect for the π-orbitals is the same as for the p_σ-orbitals, although perhaps somewhat weaker. We therefore may as well concentrate on the σ-situation and give for a selection from these calculations the density difference along the molecular axis (Fig. 7). In this figure, going from (a) to (b), we see that mainly the description of the valence electron distribution at fluorine is improved, while from (b) to (c) most of the improvement is found in the description of the core electron distribution of fluorine.

Both from the calculated dipole moment and from the population analysis, it is clear that the best description is not that using an equally small number of functions for B and F, but that a description with more functions on F than on B gives a better charge distribution. In fact, the best description is obtained if the values of $\Delta\varepsilon$ for all (valence) orbitals are of the same order of magnitude.

This conclusion will have consequences for the choice of the atomic basis sets in other molecular calculations. To reach a certain level of accuracy in a molecular calculation we now seek those basis sets on the different atoms that have the same order of magnitude for $\Delta\varepsilon$. From Van Duyneveldt's [6] series of atomic basis sets (compare Table 3) we therefore may combine a boron (5, 3) set with a fluorine (7, 4) set, and so on. The same procedure can be followed for molecules with transition metals. Wheras to reach a certain degree of accuracy for vanadium the basis set from Roos *et al.* [4], can be used, we shall have to use in the same situation Wachters' set [5] for nickel (compare Figs. 4 and 5).

In this connection one remark has to be made. Nearly all atomic basis set calculations are on the lowest state of a certain configuration. In molecular calculations we are not interested in that specific state, but in a situation that in general will be much closer to the averaged configuration. Therefore it would be preferable to publish atomic basis set calculations for averaged configurations. Even closer to the situation in a molecule is the valence state configuration instead of the ground state configurations. It would therefore be most profitable for use in molecular calculations if these atomic calculations to obtain optimal basis sets, would – also – be performed for the valence state configuration. However, the influence of these changes on the results of molecular calculations will not be as large as the influence of an unbalanced basis set.

Conclusions

From the previous sections we may summarize the following conclusions:

The quality of optimized atomic basis sets depends, for atoms in the same row of the periodic system, not only on the number of basis functions, but also on the number of valence electrons.

Basis sets built up from small atomic basis sets of the same size for atoms at the beginning and at the end of atoms of the periodic system are unbalanced and usually lead to a severe deformation in the calculated charge distribution.

In order to obtain a balanced basis set in molecular calculations more basis functions have to be used for an atom at the end of a row of the periodic system than for an atom at the beginning of the row.

A simple method to find a balanced basis set is to select the atomic basis sets in such a way that the $\Delta\varepsilon$-values for all (valence) orbitals are of the same order of magnitude.

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