Medium-Sized Gaussian Lobe Bases for Use in Molecular SCF-MO-Calculations

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Medium sized basis sets of Gaussian Lobe functions for use in SCF-MO calculations are presented. With these, computations are performed on the hydrides of the atoms Li—F. Partly, mixed bases are applied in which the one-electron integrals are calculated with respect to a more extensive basis than the two-electron integrals. The energy shifts caused by shortening of the bases are separated into several components which are discussed in detail. Some conditions are given for that cases in which mixed basis calculations yield better results for energy and virial coefficient than uniform ones. These conditions are fulfilled by the function sets proposed.

I. Introduction

Most current ab-initio-calculations of molecules are based on Cartesian Gauss functions, (GTO) which are contracted to groups[1]. In some cases, Gaussian-Lobe Functions are applied[2]. These differ from the Cartesian functions mainly in that the p-functions are represented by the difference between two primitive Gauss functions with the same exponent but displaced relative to each other. For the calculation of larger molecules it is necessary to reduce the basis size of the known accurate function sets (GTO:[3] e.g.; Lobe-Fct.:[4,5]). In the last few years there have been published a number of such expansions for GTO (Ref. [6,7] for example), whereas the reduction of Lobe-Functions has been dealt with only in two recent papers[8,9]. In the present paper basis expansions of Whitten's Lobe Functions are discussed which are smaller than the function sets of Whitten[5] and larger than those of Brown et al.[8] and Grimmelmann and Chesick[9].

One of the main tasks of this work is to study the influence of basis contraction on the different parts of the total energy. The other important point is the question whether the use of "mixed bases" will reduce the energy shifts with respect to the original basis.

In mixed basis calculations, only the time-consuming two-electrons integrals are calculated with a shortened basis, whereas for the one-electron integrals are calculated with a shortened basis, whereas for the one-electron integrals the extensive original basis is used. To answer the above questions a series of test calculations were performed for the first-row hydrids. The results are compared with those of the extensive work of Hehre et al.[7,10].

A shortened basis yields at first a variation of the matrix elements of the Hamiltonian, δH. Hence follows a redistribution of the electrons which may be characterized by a variation of the population matrix, δP. The resulting energy shift δE may thus be split into two parts δE_{H} and δE_{p} produced solely by a change of H or P, respectively. These parts may be determined by computations using the unaltered P-matrix of calculations with unshortened bases. On the other hand, these parts may be obtained by mixed- and uniform-basis calculations assuming that δP is only a first-order perturbation of P. By comparing both methods one gets knowledge whether this assumption is justified. In the latter case there will be no influence of δP on the total energy E_{tot}. The approximate fulfilment of this condition is one of the criterions for a sufficiently good basis contraction. Other conditions to be fulfilled approximately are the constancy of the ratios of one-electron-energy to two-electron-energy and of kinetic energy to potential energy.

Beyond this, the partition of the energy shift δE permits a detailed analysis of the influence of mixed bases. Mixed bases were originally suggested by Cook and Palmieri[11]. In more recent papers, Johansen[12], Brown et al.[8], and Cook et al.[13] used relatively small bases for the more-centre integrals. The latter authors criticized the consistent underestimation of the electron repulsion energy leading to unreliable results. The present paper investigates whether this is true for our greater basis sets.

The following abbreviations are used for bases or contractions: (10 5) stands for a basis of 10-s-type Gaussian and 5 p-type lobe pairs. [3; 2] means a contraction to 3 s-type and 2 p-type groups. The

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type of contraction is characterized, for example, by (3 3 4; 4 1). The numerals before the semicolon indicate the number of Gaussians in each of three different s-type groups, s_{I} (short range group, according to Whitten), s_{II} (long range), and s_{III} (intermediate range), and those following the semicolon denote the lobe pairs in the p-type groups (or group). The original Whitten functions consisted of a (10 5)-basis contracted to (3 3 4; 4 1) and (3 3 4; 5) for the atoms of the first period. Brown et al., however, used for C, N and O a much smaller (5 2) or (5 3) basis contracted to [3; 1] and Grimmelmann and Chesick a (3 2)-basis contracted to [2; 1]. The basis expansion which we describe in Section II is a contraction from (9 4), ... (6 3) to [3; 2] and [3; 1]. The results of the calculations are found in Section IV and Section V for uniform and mixed bases, respectively. Section III includes some details of the program which we devised and applied.

II. Expansion of the Basisfunctions

The function sets for the atoms of the first period were obtained from the original Whitten functions through maximization of their 3-dimensional overlap. The parameters of the new functions were calculated by means of the gradient method of Fletcher and Powell [14]. All computations were carried out with double precision on an IBM 7040. The results are given in Table 1 (for s-functions) and Table 2 (for p-functions). The last column of each Table shows the deviation η_i of the overlap from unity:

$$\eta_i = \frac{\langle a_i \mid a_i \rangle - \langle a_i \mid a_i' \rangle}{\langle a_i \mid a_i \rangle}$$

$a_i(\boldsymbol{r})$: atomic orbital number i, represented as a group of Whitten functions;

$a_i'(\boldsymbol{r})$: atomic orbital number i, represented as a smaller group of Gaussians.

Table 1. Parameters of the s-function expansion; α_i: exponential coefficients; c_i: linear combination coefficient of the i-th Gaussian; η: see text.

atom	group	α_1	α_2	α_3	c_1	c_2	c_3	$\eta\ [10^{-4}]$
Li	s I 3/2	35.2487	228.990		1.01605	0.149004		0.51
	s II 3/2	0.020024	0.051474		0.416532	1.67011		48.2
	s III 4/3	0.60059	1.96238	7.55179	1.41519	2.21077	1.06882	0.16
	s III 4/2	0.89775	4.69383		2.58433	2.03914		15.4
Be	s I 3/2	66.9382	436.091		1.01606	0.148000		0.51
	s II 3/2	0.044474	0.12710		0.657786	1.44416		39.6
	s III 4/3	1.14465	3.71727	14.2446	1.36381	2.22336	1.04503	0.16
	s III 4/2	1.72824	8.83444		2.54856	2.01385		15.0
B	s I 3/2	109.537	713.769		1.01596	0.147024		0.50
	s II 3/2	0.080024	0.23529		0.688842	1.40714		39.6
	s III 4/3	1.86943	6.09802	23.1928	1.37181	2.18931	1.02472	0.16
	s III 4/2	2.79132	14.2722		2.51456	2.00250		14.8
C	s I 3/2	161.729	1052.26		1.01593	0.147354		0.50
	s II 3/2	0.12549	0.37248		0.713601	1.35066		37.8
	s III 4/3	2.76246	8.98153	34.2109	1.36571	2.21033	1.02379	0.16
	s III 4/2	4.14223	21.0416		2.52685	2.00406		14.7
N	s I 3/2	221.420	1439.27		1.01589	0.147396		0.50
	s II 3/2	0.17771	0.53941		0.730456	1.34606		36.8
	s III 4/3	3.79315	12.3033	46.8468	1.33195	2.20890	1.02308	0.16
	s III 4/2	5.73717	28.9642		2.50436	1.99123		14.7
O	s I 3/2	294.639	1915.58		1.01589	0.147299		0.50
	s II 3/2	0.24295	0.74455		0.741833	1.33604		35.3
	s III 4/3	5.04342	16.3419	62.2408	1.34166	2.22141	1.01986	0.16
	s III 4/2	7.61556	38.3463		2.51844	1.99599		14.9
F	s I 3/2	371.250	2413.21		1.01584	0.146956		0.49
	s II 3/2	0.30766	0.96743		0.747855	1.41120		36.2
	s III 4/3	6.37999	20.6001	78.4391	1.29894	2.22206	1.01902	0.16
	s III 4/2	9.74666	48.6596		2.49289	1.97947		14.4
Ne	s I 3/2	469.396	3057.01		1.0587	0.146433		0.50
	s II 3/2	0.38922	1.22294		0.754681	1.39462		34.5
	s III 4/3	8.03803	25.9980	98.9562	1.33644	2.23068	1.01440	0.16
	s III 4/2	12.1544	60.8537		2.51938	1.99383		14.5

Table 2. Parameters of the p-function expansions; α_i: exponential coefficients, c_i linear combination coefficients of the i-th lobe pair, Δr_i displacement of the origin of Gaussian in the i-th lobe pair. η: see text.

atom	α_1	α_2	α_3	α_4	c_1	c_2	c_3	c_4	Δr_1	Δr_2	Δr_3	Δr_4	$\eta\ [10^{-4}]$
B p 5/4	0.075424	0.24862	0.88079	3.93000	216.3779	208.1709	62.2405	8.10735	0.12576	0.10954	0.09718	0.08159	0.25
p 5/3	0.077386	0.27386	1.24341		227.6147	214.1654	51.9489		0.12509	0.10880	0.09291		9.03
p 4/3	0.24724	0.87096	3.86383		208.0817	62.8786	8.32619		0.10959	0.09739	0.08173		0.44
p 4/2	0.25553	1.13759			218.9974	58.7846			0.10946	0.09378			19.0
C p 5/4	0.12178	0.41726	1.49119	6.58230	217.3376	209.1783	62.9860	8.09810	0.09897	0.08455	0.07462	0.06317	0.22
p 5/3	0.12465	0.45645	2.07405		227.2239	215.7695	53.4393		0.09845	0.08396	0.07155		9.02
p 4/3	0.41522	1.47626	6.47970		209.0663	63.5444	8.30185		0.08459	0.07470	0.06326		0.40
p 4/2	0.42879	1.91429			219.7011	59.7236			0.08446	0.07214			18.5
N p 5/4	0.17603	0.62133	9.69385	2.24255	219.4412	207.0803	8.18383	62.8164	0.08228	0.06955	0.05217	0.06112	0.22
p 5/3	0.17986	0.67695	3.09710		228.3988	213.9200	54.0523		0.08188	0.06905	0.05872		8.97
p 4/3	0.61851	2.22119	9.54784		206.9566	63.3197	8.38594		0.06959	0.06118	0.05225		0.38
p 4/2	0.63855	2.87538			217.3269	59.8750			0.06946	0.05916			18.4
O p 5/4	0.21257	0.71018	2.45207	10.65976	155.8758	204.2740	84.8181	14.3137	0.11759	0.07549	0.06368	0.04877	0.40
p 5/3	0.22602	3.91311	0.84406		175.0853	66.2852	216.196		0.11317	0.05834	0.07367		14.6
p 4/3	0.70536	2.42731	10.53782		204.0820	85.6263	14.5838		0.07558	0.06377	0.04888		0.67
p 4/2	0.74784	3.43942			223.2911	78.6350			0.07531	0.05940			30.3
F p 5/4	0.25924	0.88391	3.10335	13.74783	150.4308	198.7093	86.2569	14.6562	0.10492	0.06762	0.05715	0.04329	0.39
p 5/3	0.27629	1.05605	4.94784		169.2568	211.0472	67.9159		0.10086	0.06606	0.05224		17.3
p 4/3	0.87847	3.07646	13.61366		198.5567	86.9562	14.8878		0.06769	0.05722	0.04337		0.62
p 4/2	0.93366	4.35851			217.7611	80.1372			0.06749	0.05320			34.4
Ne p 5/4	0.33221	1.13323	3.97774	17.63149	153.4606	196.1686	86.6019	14.6096	0.09264	0.05973	0.05049	0.03821	0.39
p 5/3	0.35353	1.35647	6.32834		172.1653	208.6924	68.1502		0.08914	0.05835	0.04617		17.3
p 4/3	1.12616	3.94342	17.45902		196.0152	87.3015	14.8409		0.05979	0.05056	0.03829		0.63
p 4/2	1.19776	5.57553			215.2230	80.4336			0.05961	0.04701			34.6

Although there is no direct relationship between η_i and the quality of the approximate orbitals, this parameter can be used as a criterion for the accuracy of a particular expansion.

The expression sI 3/2, for example, denotes the first s-group of an atom with originally 3 and now 2 functions. p 5/5 stands for Whitten's p-group with 5 lobe pairs, whereas for p 4/4 from the same group the most extensive function has been removed and treated as a separate group. As can be seen from Table 1, the sI 3/2 and sIII 4/3 expansions are very good approximations of the initial functions, whereas the deviations of the sIII 4/2 groups are two powers of ten larger. The 2-term expansion of the sII 3/3 group is even worse because sII 3/3 is not a monotonous function of r (Figure 1).

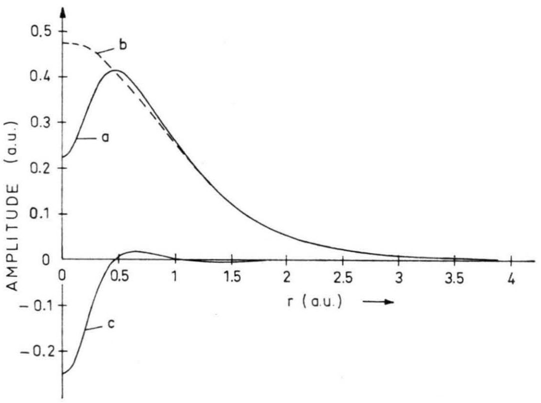

Fig. 1. sII orbital for 0 as a function of the distance r from the nucleus: a) Whittens normalized 3-term group sII 3/3 (r); b) 2 term expansion sII 3/2 (r) (this work); c) $\delta(r) = \text{sII } 3/3\,(r) - \text{sII } 3/2\,(r)$.

Among the p-groups, there is only a very small deviation from Whitten's groups for the p 5/4 and p 4/3 expansions, but the η-values for p 5/3 and p 4/2 are each $40-50$ times as large. However, because a p 5/3-basis contains 6 primitive Gauss functions per atom less than a p 5/4 basis, it will be necessary to use the p 5/3 expansions in order to decrease calculation time in the case of larger molecules. According to Table 2, the p 5/3-group gives better results than the p 4/2 + p 1-group.

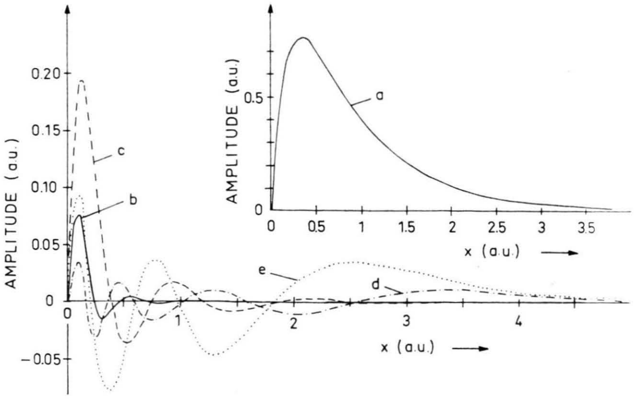

Fig. 2. p-orbital for 0 along the x-axis. a) Whittens normalized 5-term group p 5/5 $(x, 0, 0)$; b) $\delta_1(x) = \text{p } 5/5\,(x, 0, 0) - \text{p } 5/4\,(x, 0, 0)$ with the 4-terms expansion p 5/4 (this work); c) $\delta_2(x) = \text{p } 5/5\,(x, 0, 0) - \text{p } 5/3\,(x, 0, 0)$ with a 3-term expansion p 5/3 (this work); d) $\delta_3(x) = \text{p } 5/5\,(x, 0, 0) - \text{p } 5/3\,(x, 0, 0)$ with a 3-term expansion p 5/3 (Brown et al. [8]); e) $\delta_4(x) = \text{p } 5/5\,(x, 0, 0) - \text{p } 5/2\,(x, 0, 0)$ with the 2-term expansion p 5/2 (Brown et al. [8]).

Figure 2 shows a section through the p 5/5-group of an O-atom as well as the deviations of our expansion from this orbital. The deviations of the expansion of Brown et al. [8] for the same function are also shown. The latter gives a better depiction of the function than our approximation for small values of x, however, for distances from the nucleus which correspond to molecular bond lengths, the deviations of our functions are smaller. We suppose that the function parameters of Brown et al. were obtained through adjustment to the radial part of Whitten functions, whereas we maximized the three-dimensional overlap. If, instead of the above noted cut through the reduced groups, we now consider the radial electron density, $w(r) \approx r^2 \cdot f^2(r)$, where

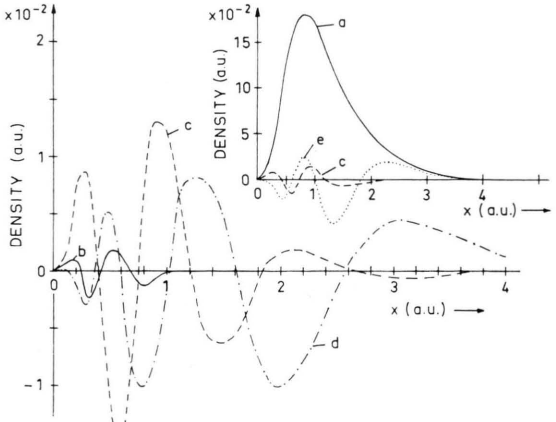

Fig. 3. Radial electron density of the p-orbital for 0; a) with respect to Whittens p 5/5-group; b) difference between a and the density calculated with respect to the p 5/4 contraction (this work); c) difference between a and the density calculated with respect to the p 5/3 contraction (this work); d) difference between a and the density calculated with respect to the p 5/3 contraction (Brown et al. [8]); e) difference between a and the density calculated with the p 5/2 contraction (Brown et al. [8]).

$f(r)$ is the radial part of the functions *, we find a uniformly good agreement between the electron density obtained from our expansion and that from the Whitten-functions (Figure 3). The values proposed by Brown et al., however, give larger deviations for large r.

It is to be expected that, due of the different type of adaption, the functions of Brown et al. are well suited for 1-electron properties concerned with the nucleus, but that regions further from the nucleus and thus also chemical bonds are better described by our functions.

III. Some Details of the Program

All molecular calculations were carried out with a SCF-LCAO-MO program which was written by us. Major characteristics of the program are:

1. A simulation program can be placed before the calculation of the integrals. In this program – as in a similar one suggested by ROTHENBERG and others [16] – simplified calculations are done for all 2-electron integrals in which each group is represented by a single function (or two for p-groups). These results reflect fully the symmetrical behavior of the actual integrals. Repetitious calculation of integrals which occur more than once can thus be avoided through comparison of the simplified values. Particularly integrals which disappear are recognized immediately. Much time can be saved through this procedure in the calculation of symmetrical molecules (in the case of NH_3, for example, 45%).

2. The program contains a special symmetry part (a communication dealing with a similar program has recently been independently published by SIEGBAHN [17]) for all molecules which possess a C_2-axis, a center of inversion or a plane of symmetry. Suppose we have a molecule with a C_2-axis, then:

$$(i\,j\,|\,k\,l) = (i'\,j'\,|\,k'\,l')$$

with $i' = C_2\, i$, and so forth. The symmetry program prevents the calculation of the second integral and carries over the value of the first. In this way, the time needed to calculate the integrals can be halved. Other than a few parameters, this program does not require any further input data.

3. The function

$$F(s) = \frac{2}{s\sqrt{\pi}} \int_0^s e^{-t^2}\, \mathrm{d}t$$

which occurs during the calculation of the integrals was expressed by a new expansion in the interval $0 < s^2 < 16$; for $s^2 > 16$ it was replaced by $F(s) = 1/s$. The new expansion is a 16-part Tschebyscheff expansion which was transformed into a polynome $P_0(s^2)$. The polynomes are of degree 3 to 6; a maximum error $|\Delta F| < 10^{-7}$ is attained. Compared to other expansions [18], the new method requires definitly less calculating time. When tabulating the function and interpolating quadratically the time of calculation decreased only insignificantly, but the amount of storage space needed was greatly increased.

4. In the SCF-part, the pseudo-eigenvalue equation $F\,C = \varepsilon\, S\, C$ is converted, after a Cholesky transformation of the overlap matrix, to the standard form $F'\,C' = \varepsilon\, C'$, which is solved by a QR-algorithm [19]. After three iterations in each case, a somewhat modified form of Aitkens' δ^2 procedure is applied to accelerate convergence and prevent divergence. Convergence is obtained when the variation of each element of the P-matrix is below a previously set limit. For a value of 10^{-6} in general this occurs after 10 – 20 iterations.

IV. Uniform Bases

To test the quality of the new basis expansions some test calculations were made for the hydrids of the first-row atoms. Some results are listed in Tables 3 – 5 in the rows or columns marked by "uniform". In addition to the total energies, the atomisation energies and dipole moments are stated, as a test of the accuracy with which small energy differences are rendered by the invididual bases. The atomisation energies are a very sensitive test because the electron charge on the atom and thereby the population matrix P change greatly when the molecule is split. The dipole moments reflect the occuring charge densities. As a comparison to our result, data are stated which HEHRE and others [10] obtained through similar basis expansions with the scaling factors $\xi = \sqrt{1.8}$ for CH_4, $\xi = \sqrt{1.65}$ for H_2O and $\xi = \sqrt{1.6}$ for the rest of the atoms. Experimentally obtained molecular geometry [21] was used for all calculations.

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* Because the lobe-p-function cannot be described exactly as a product of radial part and harmonic functions, so w for the p-functions is not a pure radial function. The deviations are very small, however, and can be neglected here [15].

Table 3. Total energies of the first row hydrids (a. u.).

basis[a]		LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	FH
(3 3 4; 4 1)[b]		– 7.95532	– 15.64852	– 26.3682	– 40.1801	– 56.1706	– 76.0012	– 100.0098
(2 3 3; 3 1)[b]	unif.	.95233	.64305	.3569	.1575	.1424	– 75.9499	– 99.9342
	mixed	.95636	.64973	.3706	.1798	.1738	– 76.0073	– 100.0184
(3 3 4; 5)		—	—	.3536	.1756	.1523	– 75.9818	– 100.0000
LEMAO-5 G[c]		—	—	—	.1642	.1366	.9693	– 99.9868
(2 3 3; 4)	unif.	—	—	.3426	.1511	.1239	.9296	– 99.9232
	mixed	—	—	.3559	.1787	.1558	.9877	– 100.0095
LEMAO-4 G[c]		—	—	—	.1213	.0729	.8790	– 99.8655
(2 3 3; 3)	unif.	—	—	.3247	.1114	.0360	.7568	– 99.6321
	mixed	—	—	.3699	.2053	.2112	– 76.0948	– 100.1840
LEMAO-3 G[c]		—	—	—	– 39.9358	– 55.7997	– 75.4990	– 99.3573
HF-energy		– 7.99[d]	– 15.78[e]	—	– 40.23[f]	– 56.23[f]	– 76.6[f]	– 100.07[d]

[a] The basis for hydrogen not included in the first column is always a (3 1) s-type basis [20]; [b] for Li and Be there are no p-type orbitals in the basis; [c] values of HEHRE, DITCHFIELD, and POPLE [10]; [d] Ref. [24]; [e] Ref. [22]; [f] Ref. [25].

Table 4. Atomisation energies of the first row hydrids (a. u.).

basis[a]		LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	FH
(3 3 4; 4 1)		0.0241	0.0783	0.3428	0.4940	0.2831	0.2103	0.1239
(2 3 3; 3 1)	unif.	0.0241	0.0783	0.3415	0.4884	0.2814	0.2086	0.1224
	mixed	0.0241	0.0782	0.3439	0.4913	0.2830	0.2099	0.1241
(3 3 4; 5)		—	—	0.3294	0.4926	0.2665	0.1921	0.1172
(LEMAO-5 G)				—	0.4917	0.2582	0.1909	0.1188
(2 3 3; 4)	unif.	—	—	0.3287	0.4854	0.2643	0.1896	0.1147
	mixed			0.3299	0.4932	0.2665	0.1923	0.1174
LEMAO-4 G				—	0.4946	0.2591	0.1898	0.1172
(2 3 3; 3)	unif.	—	—	0.3207	0.4800	0.2543	0.1770	0.1097
	mixed			0.3333	0.4937	0.2711	0.1966	0.1207
LEMAO-3 G				—	0.5043	0.2605	0.1884	0.1153
experimental[b]		0.0935	not known	0.360	0.627	0.3605	0.350	0.2155

[a] Notation see Table 3; [b] Ref. [26].

Table 5. Dipole moments (Debye).

basis[a]	(3 3 4; 4 1)	(2 3 3; 3 1) unif.	(2 3 3; 3 1) mixed	(3 3 4; 5)	(LEMAO-5 G)	(2 3 3; 4) unif.	(2 3 3; 4) mixed	(LEMAO-4 G)	(2 3 3; 3) unif.	(2 3 3; 3) mixed	(LEMAO-3 G)	Exper.[27]
FH	2.47	2.45	2.48	2.20	2.46	2.16	2.23	2.42	1.87	2.43	2.23	1.82
H_2O	2.72	2.70	2.72	2.47	2.72	2.46	2.48	2.70	2.18	2.65	2.51	1.85
NH_3	2.36	2.37	2.37	2.25	2.23	2.23	2.26	2.21	2.08	2.35	2.07	1.47
LiH	4.57	4.57	4.59	—	—	—	—	—	—	—	—	5.88

[a] Notation see Table 3.

The following nuclear distances were used for the instable molecules BeH_2 and BH_3: $r_{\mathrm{Be-H}} = 1.35$ Å [22]; $r_{\mathrm{B-H}} = 1.22$ Å (plane configuration) [23].

The following conclusions can be drawn from the data in Tables 3 to 5 (in the rows or columns dealing with uniform bases):

1. The total energies which we calculated are lower than those which Hehre et al. reported for comparable bases. In addition, our values are less dependent on the choice of basis.

2. The atomisation energies are smaller than the experimental values, as is true for other single-

determinant LCAO-MO-calculations[10]. They vary less with a change of basis in the calculations of HEHRE et al.[10], than in our calculations. This difference is probably due mainly to the fact that the above named authors optimized the scaling factors of all atoms for each basis, whereas we used constant scaling factors.

3. The values of the dipole moments decrease weakly when shortening the basis. This effect is in agreement with the results of Hehre et al. It is confirmed that the dipole moment of all molecule will not be accurately determined from energy optimized Gauss functions.

The energy shift as a function of the basis can be more thoroughly discussed with the aid of Table 6 (values for uniform bases), which specifies the various contributions to the toal energy E_{tot} for bases with only one p-group.

$$E_{\text{tot}} = E_1 + E_2 + V_{\text{nucl}}; \quad E_1 = T + V_{\text{en}} \qquad (1)$$

where: E_1 = one electron energy (T: kinetic energy, V_{en}: electron-nucleus attraction energy); E_2: two electron repulsion energy; V_{nucl}: nucleus-nucleus repulsion energy. δT, the kinetic energy shift with respect to reduction of the basis, is given by $\delta T = T$ (small basis) $- T$ (large basis). The other energy shifts are defined analogously. H_2O has been chosen as an example, but similar results were obtained for all other molecules. Noteworthy is the fact that, by the variation of several AO's the total change of all energy components is very close to the sum of the changes for the single AO's. This indicates that for all expansions the errors are so small that only linear effects are significant and that second and higher order perturbations can be neglected. Therefore, in the following only those effects need to be observed which are caused by changing single AO's. Another important fact is that $|\delta E_1|$ is always larger than $|\delta E_2|$.

For a better analysis of the errors introduced by the shortened bases the above mentioned energy parts are discussed in detail, using H_2O as an example. In order to separate the effects caused by changes of the P-matrix from those due to shifts of the matrix elements of the Hamiltonian alone, some calculations have been carried out in which the P-matrix was obtatined from the results with respect to the unshortened basis. The matrix elements of the Hamiltonian were determined from the new functions.

Tables 7 and 8 show that:

1. The values of δE_{tot} calculated with respect to a constant P-matrix and to one changed after passing the SCF-part differ only very little. This is true for all basis expansions presented here.

2. The energy shifts δE_{p} and δE_{H} are of the same order of magnitude. $\delta E_{1\text{p}}$ and $\delta E_{2\text{p}}$ nearly compensate themselves.

Table 6. Contributions to the total energy of H_2O (a. u.), $V_{\text{nucl}} = 9.2400$.

Basis[a] (3 3 4; 5)		T 76.0992	V_{en} -199.6512	E_1 -123.5520	E_2 38.3302	E_{tot} -75.9818
		δT $[10^{-4}]$	δV_{en} $[10^{-4}]$	δE_1 $[10^{-4}]$	δE_2 $[10^{-4}]$	δE_{tot} $[10^{-4}]$
(2 3 4; 5)	unif.	-355	$+459$	$+104$	-8	$+96$
	mixed	$+60$	-68	-8	-11	-19
(3 3 3; 5)	unif.	$+1431$	-1320	$+111$	$+31$	$+142$
	mixed	$+65$	-50	$+15$	-10	$+5$
(2 3 3; 5)	unif.	$+1081$	-867	$+214$	$+24$	$+238$
	mixed	$+126$	-118	$+8$	-22	-15
(3 3 4; 4)	unif.	-514	$+1231$	$+717$	-430	$+287$
	mixed	$+73$	-183	-110	$+51$	-60
(2 3 3; 4)	unif.	$+568$	$+363$	$+931$	-407	$+524$
	mixed	$+200$	-302	-102	$+28$	-75
(3 3 4; 3)	unif.	-4104	$+9762$	$+5658$	-3643	$+2015$
	mixed	$+1198$	-3170	-1972	$+838$	-1134
(2 3 3; 3)	unif.	-3020	$+8891$	$+5871$	-3620	$+2251$
	mixed	$+1323$	-3285	-1962	$+814$	-1148

[a] Notation see Table 3.

Table 7. Shifts of energies and virial coefficients for H_2O (in units of 10^{-4}).

modif.[a] AO	$\delta E_\text{tot}/\lvert E_\text{tot}\rvert$		$\frac{\delta E_\text{tot, H}}{\lvert E_\text{tot}\rvert}$	$\delta(-E_1/E_2)_\text{H}$		δVir_H		δVir_p		δVir	
	unif.	mixed		unif.	mixed	unif.	mixed	unif.	mixed	unif.	mixed
s I 3/2	1.3	− 0.2	1.4	1,9	− 1.1	− 0.1	0.1	1.8	− 0.4	1.7	− 0.3
s III 4/3	1.9	+ 0.1	2.6	5.5	− 0.5	10.7	0	− 20.8	− 0.5	− 10.1	− 0.5
p 5/4	3.8	− 0.8	3.7	− 18	+ 1.6	0.4	0.4	1.2	− 0.5	1.6	− 0.1
p 5/3	26.5	− 15	24	− 158	+ 19	7.1	7.4	6.4	− 7.8	13.5	− 0.4

Vir (large basis) = 0.99923; $Vir = -V/2T$. — [a] Changes with respect to (3 3 4; 5) basis of WHITTEN[5].

3. $\delta(E_1/E_2)$ and δVir are of the same order of magnitude as

$$\delta E_\text{tot}/E_\text{tot} \quad (\text{virial coefficient } Vir = -V/2T).$$

Besides the energy shift there is a redistribution of electrons when changing the basis functions. In Table 10, dipole moments and the occupation numbers of the most affected AO's are listed. It is seen that the density shift is significantly larger for reduction of p-orbitals than of s-orbitals. The electrons flow mainly from the p-orbitals to the s-orbitals of the H-atoms; these orbitals show a large overlap population. For the deep energy s-orbitals of the heavy nuclei there is only a small reorganisation of the occupation numbers accompanied by a relatively large energy shift.

V. Mixed Bases

The above described partition of the energy into one- and two-electron-parts shows that the major portion of the total energy shift δE which occurs by the change to reduced bases is due to a shift in the one-electron energy E_1. It therefore seems plausible to try to reduce δE through calculating E_1 with the extensive original basis and using a shortened basis only for the time-consuming two-electron integrals. Prerequisite for the application of this method is that the small groups of Gaussians approximate the respective atomic orbitals in nearly the same degree of accuracy as the large ones. This condition is fulfilled by the overlap maximisation procedure, described in Section II.

Table 3 to 5 show – in the rows or columns signified by "mixed" bases – several results obtained for the hydrids of the first row. A few of the conclusions which may be drawn are:

1. δE_tot obtained from mixed bases is smaller than that from uniform bases by a factor of approximately 2 for the (2 3 3; 3)-bases and generally by a much larger factor for all other bases.

2. The total energies calculated from mixed bases are almost always lower than the total energies obtained from unshortened bases. E_tot usually decreases when one changes from a larger to a smaller basis.

3. The atomisation energies are less dependent on the size of the basis for mixed bases than for uniform bases. The relative deviation from the (3 3 4; 5)-basis has a maximum value of 0.2% for the (2 3 3; 4)-basis (uniform basis: 2.1%) and 3% for the (2 3 3; 3)-basis (uniform basis: 8%). The values obtained by HEHRE et al.[10] from comparable bases, with 1.3% and 3% deviation, respectively, were also attained here, although the scale factors were not determined a new for each atom, as was done by the above authors.

4. The deviation in dipole moments calculated with reduced bases are similar in size but opposite in direction to those obtained when uniform bases are used.

Table 6 shows the energy shift as a function of change of single or several AO's for both uniform and mixed bases, using H_2O as an example. Most of the energy shifts for mixed bases are significantly less than the respective values for uniform bases. As before, the energy shifts due to changes of several AO's can be described as sums of energy shifts resulting from changes of individual AO's. This finding suggests that the change to shortened bases may be treated within the frame of first order perturbation theory. The reduction of the basis size causes perturbations δh, δV, and – as a consequence – δF of the Hartree-Fock matrix

$$F = h + V \bullet P\,. \tag{2}$$

h is the matrix of the one-electron Hamiltonian, based on the AO's a_i. P is the bond-order – or population matrix. The "supermatrix" V contains the two-electron components of the Hamiltonian:

$$V_{ij,kl} = (i\,j\,|\,k\,l) - \tfrac{1}{2}\,(i\,k\,|\,j\,l) = V_{kl,ij} = V_{ji,lk} = V_{lk,ji} \tag{3}$$

with

$$(i\,j\,|\,k\,l) = \int \mathrm{d}\tau_1\,\mathrm{d}\tau_2\,a_i(1)\,a_k(2)\,\frac{1}{r_{12}}\,a_1(2)\,a_j(1)\,. \tag{4}$$

The multiplication $V \bullet P$ of the "supermatrix" V with the bond-order-matrix P is defined by

$$(V \bullet P)_{ij} = \sum_{kl} V_{ij,kl}\,P_{kl}\,. \tag{5}$$

With the help of the relation

$$E_{\mathrm{el}} = \mathrm{tr}\,(P\,h) + \tfrac{1}{2}\,\mathrm{tr}\,(P\,V \bullet P) \tag{6}$$

it follows for the perturbation of the energy in the first order [28]:

$$\delta E_{\mathrm{tot}} = \mathrm{tr}\,\big(\delta P\,(h + V \bullet P)\big) + \mathrm{tr}\,\big(P\,(\delta h + \tfrac{1}{2}\,\delta V \bullet P)\big)\,. \tag{7}$$

The first term disappears because the energy has attained a minimum with respect to a variation of P:

$$\mathrm{tr}\,\big(\delta P\,(h + V \bullet P)\big) = \mathrm{tr}\,(\delta P\,F\,|_{\mathrm{p}}) = 0 \tag{8}$$

in other words:

$$\delta E_{\mathrm{tot}} = \mathrm{tr}\,\big(P\,(\delta h + \tfrac{1}{2}\,\delta V \bullet P)\big)\,. \tag{9}$$

For the energy components δE_1 and δE_2 is found:

$$\begin{aligned} \delta E_1 &= \delta E_{1,\mathrm{H}} + \delta E_{1,\mathrm{P}} = \delta T_{\mathrm{H}} + \delta V_{\mathrm{en,H}} + \delta T_{\mathrm{p}} \\ \delta E_2 &= \delta E_{2,\mathrm{H}} + \delta E_{2,\mathrm{P}} + \delta V_{\mathrm{en,P}} \end{aligned} \tag{10}$$

with the abbreviations:

$$\begin{aligned} \delta E_{1,\mathrm{H}} &= \mathrm{tr}\,(P\,\delta h)\,, \\ \delta E_{1,\mathrm{p}} &= \mathrm{tr}\,(\delta P \cdot h)\,, \\ \delta E_{2,\mathrm{H}} &= \tfrac{1}{2}\,\mathrm{tr}\,(P\,\delta V \bullet P)\,, \\ \delta E_{2,\mathrm{p}} &= \mathrm{tr}\,(\delta P\,V \bullet P)\,. \end{aligned} \tag{11}$$

Therefore from (8):

$$\delta E_{1,\mathrm{p}} = -\,\delta E_{2,\mathrm{p}} \tag{12}$$

and from (9):

$$\delta E_{\mathrm{tot}} = \delta E_1 + \delta E_2 = \delta E_{1,\mathrm{H}} + \delta E_{2,\mathrm{H}} \tag{13}$$

(i. e. E_{tot} is independent of δP in first-order perturbation theory).

For mixed bases

$$\delta h = 0 \tag{14}$$

and therefore:

$$\delta E^{\mathrm{m}}_{\mathrm{tot}} = \delta E_{2,\mathrm{H}}\,, \tag{15}$$

$$\delta E^{\mathrm{m}}_{1} = \delta E^{\mathrm{m}}_{1,\mathrm{P}}\,. \tag{16}$$

To distinguish between mixed and uniform bases, the respective values are characterized by the index m and u. From the above equations it follows

$$\delta E_{1,\mathrm{H}} = \delta E^{\mathrm{u}}_{\mathrm{tot}} - \delta E^{\mathrm{m}}_{\mathrm{tot}}\,, \tag{17}$$

$$\delta E^{\mathrm{u}}_{1,\mathrm{P}} = \delta E^{\mathrm{u}}_{1} + \delta E^{\mathrm{m}}_{\mathrm{tot}} - \delta E^{\mathrm{u}}_{\mathrm{tot}}\,. \tag{18}$$

With the help of Eqs. (15) through (18), the first order energy shift can be separated into components which are due only to changes δh, δV or δP. On the other hand this partition can be done by direct calculations as in Section IV. There the energy is calculated with respect to the bond-order matrix resulting from the calculations with an unshortened basis. Thus, by comparing the results of both methods, we have a criterion for the validity of the firster order parturbation formalism. The changes of total energy and of some ratios of parts of the energy are given in Table 7. Table 8 shows some values calculated directly by keeping the P-matrix constant. Table 9 gives some energy shifts calculated independently from Table 8 according to Eqs. (12) to (18).

The following information can be drawn from the Tables:

a) For all basis variations considered here, the energy shifts calculated according to perturbation formalism agrees very well with the value resulting from the direct calculations (compare for example

Table 8. Shifts of the energy contribution for H_2O as a function of the changes of single AO's (10^{-4} a. u.; direct calculation).

1	2	3	4	5	6	7	8	9	10
modif.[a]	δT_{H}	$\delta V_{\mathrm{en,H}}$	$\delta E_{1,\mathrm{H}}$	$\delta E_{2,\mathrm{H}}$	δT_{p}	$\delta V_{\mathrm{en,p}}$	$\delta E_{1\mathrm{p}}$	$\delta E_{2\mathrm{p}}$	
AO					unif.	unif.	unif.	unif.	mixed
s I 3/2	− 101	234	133	− 21	− 254	225	−29	13	10
s III 4/3	−1797	1966	169	3	3228	−3286	−58	28	−13
p 5/4	− 348	689	341	− 60	− 166	542	376	− 370	111
p 5/3	−3099	6252	3153	−1125	−1005	3510	2505	−2518	1963

[a] Changes with respect to the (3 3 4; 5) basis of WHITTEN [5].

Table 9. Shifts of the energy contribution for H_2O as a function of the changes of single AO's (10^{-4} a. u.), calculated with respect to Equations (12) – (18).

1 modif.[a] AO	2 δE_{1H}	3 δE_{2H}	4 δT_p mixed	5 $\delta V_{en,P}$ mixed	6 δE_{1P} mixed	7 δE_{1P} unif.
sI 3/2	115	−19	60	−68	−8	−11
sIII 4/3	137	5	65	−50	15	−26
p 5/4	347	−60	73	−183	−110	370
p 5/3	3149	−1134	1198	−3170	−1972	2509

[a] Changes with respect to the (3 3 4; 5) basis of WHITTEN[5].

column 4, 5, 8 of Table 8 with column 2, 3, 7 of Table 9). That means that the perturbation formalism described above is justified. This result is verified by the fact that Eq. (8) and (12) are fulfilled sufficiently, as is shown by comparison of columns 8 and 9 of Table 8 or column 10 of Table 8 and column 6 of Table 9.

b) Although $\delta E_{1,\mathrm{H}}$ and $\delta E_{2,\mathrm{H}}$ have different signs in most cases, it is always true that

$$|\delta E_{1,\mathrm{H}} + \delta E_{2,\mathrm{H}}| > |\delta E_{2,\mathrm{H}}| . \tag{19}$$

This means that the energy deviation resulting from a reduction of the bases is smaller for mixed bases than for uniform bases. $\delta E_{2,\mathrm{H}}$ is negative in all cases, except for the sIII function. Thus the total energy calculated with the mixed basis is lower than with the large original basis. This is no violation of the variation principle because the prerequisites of the theorem – the use of a uniform basis for all matrix elements – are not fulfilled here. The shift $\delta E_{2,\mathrm{H}} < 0$ when contracting the bases is a result of the decrease of charge density around an atomic nucleus. By reason of this fact the electron-electron repulsion in this region decreases.

c) The absolute values of the energy contribution which result solely from changes in the P-matrix are also smaller for the mixed bases than for the uniform bases. Because of Eq. (13), these components are not noticeable in the first order total energy shift. However, they change the ratio of 1-electron to 2-electron energy and thus the ratio of potential to kinetic energy.

This last effect – as well as the assumed undervaluation of E_2 when using mixed bases[13] – should also influence the virial coefficient *Vir*. Hence the last two criterions mentioned in the introduction concerning the "goodness" of a given basis expansion were not fulfilled, especially for mixed bases. However, as shown in Table 6, δE_2 is usually much smaller for mixed bases than for uniform. This holds even stronger for both $\delta(-E_1/E_2)$ and δVir (see Table 7). So the above criterions are satisfied better by the mixed bases, and the objections by COOK et al.[13] do not prove right here, at least for the molecules considered. Examining the first order variation of the virial coefficient in the energy minimum of the extended basis ($Vir = 1$) yields:

$$\delta Vir = -\frac{V}{2\,T}\left(\frac{\delta V}{V} - \frac{\delta T}{T}\right) = -\frac{1}{2\,|E_{\mathrm{tot}}|}\,(\delta V + 2\,\delta T)$$
$$= -\frac{1}{2\,|E_{\mathrm{tot}}|}\,(\delta E_{\mathrm{tot}} + \delta T_{\mathrm{H}} + \delta T_{\mathrm{p}}) . \tag{20}$$

For mixed bases this reduces to:

$$\delta Vir = -\frac{1}{2\,|E_{\mathrm{tot}}|}\,(\delta E_{2,\mathrm{H}} + \delta T_{\mathrm{p}}) . \tag{21}$$

The occurrence of δT_{p} in Eqs. (20), (21) shows the effect of changes of the electron density on the virial coefficient. Table 7 shows that the electron distribution with respect to mixed bases varies in such a way that the virial coefficient is hardly changed; $\delta E_{2\mathrm{H}}$ is nearly compensated by δT_{p}. A comparison of values for dipole moments and occupation numbers of some AO's (Table 10) shows an opposite direction of the charge shift for the two methods. A population analysis clarifies that the charge shift is towards the H-atoms for uniform bases and away from the H-atoms for mixed bases. As was found fr the virial coefficients and most of the parts of the energy, the absolute value of the changes in dipole moment and occupation number are smaller for mixed bases than for uniform bases.

Table 10. Variations of the electronic dipole moment μ_{el} (a. u.) and of the occupation numbers n (sIII) and n(p) for H_2O.

Basis[a]		$-\mu_{\mathrm{el}}$	n(s III)	n(p)
(3 3 4; 5)		1.229	1.9566	4.912
(2 3 4; 5)	unif.	1.229	1.9568	4.912
	mixed	1.229	1.9565	4.912
(3 3 3; 5)	unif.	1.229	1.9550	4.911
	mixed	1.228	1.9565	4.913
(3 3 4; 4)	unif.	1.245	1.9566	4.904
	mixed	1.224	1.9566	4.921
(3 3 4; 3)	unif.	1.343	1.9566	4.807
	mixed	1.146	1.9566	4.966

[a] Notation see Table 3.

The underestimation of E_2 in calculations using mixed bases has proved to be not serious in all cases examined; on the contrary most changes are considerably smaller with mixed bases. Just so, with our relatively large basis sets there could be detected no change in the order of orbital energies, as reported by COOK et al.[13] for benzene. As an example, Table 11 shows the orbital energies of formic acid, computed with respect to Whitten's original basis and to our smallest one (mixed fashion). For comparison the values of $\delta E_{1\mathrm{H}}$ and $\delta E_{2\mathrm{H}}$ are included.

Table 11. A comparison of orbital and total energies for formic acid using two different basis sets (a. u.).

(3 3 4; 5) (Whitten's original basis[5])	(2 3 3; 3) (mixed basis)
−20.5838	−20.5792
−20.5359	−20.5432
−11.5521	−11.5711
− 1.5706	− 1.4670
− 1.3705	− 1.3496
− 0.9226	− 0.9139
− 0.7602	− 0.7337
− 0.6981	− 0.6829
− 0.6598 π	− 0.6518 π
− 0.5660	− 0.5816
− 0.4801	− 0.5016
− 0.4713 π	− 0.4849 π
0.1441 π	0.1207 π
0.3389	0.3241
$E_{\mathrm{tot}} = -188.5358$	$E_{\mathrm{tot}} = -188.6981$
$\delta E_{2,\mathrm{H}} = -0.1623$	$(\delta E_{1,\mathrm{H}} = 0.6627)$

VI. Conclusions

It has been shown that the new basis expansions fulfill the conditions for sufficiently good bases mentioned in the introduction: a) the shortening of the basis leads to only first-order perturbations of the energy compared with the original basis; b) the change of the ratio of one- to two-electron energy is only of the same order of magnitude as $\delta E/E$; c) the same is true for the ratio of kinetic to potential energy.

As a consequence of the first condition, the total energy is nearly independent of the electron shift generated by the change of basis. Moreover, one gets the total energy shift when changing several AO's simultaneously by adding the energy shifts produced by changing only one AO.

Under the assumption that the second criterion $\delta(E_1/E_2) \approx 0$ is fulfilled exactly for the changes introduced by the variation of the matrix elements of the Hamiltonian, one has

$$\delta E_{1,\mathrm{H}}/\delta E_{2,\mathrm{H}} = E_1/E_2 \tag{22}$$

and

$$\delta E_{1,\mathrm{H}} + \delta E_{2,\mathrm{H}} = (1 + (E_1/E_2)) \cdot \delta E_{2,\mathrm{H}} \,. \tag{23}$$

Since for all molecules:

$$E_1/E_2 < -2 \tag{24}$$

(for the hydrids of the atoms of the first row: $E_1/E_2 \approx -3$) there is

$$|\delta E_{1\mathrm{H}} + \delta E_{2\mathrm{H}}| > |\delta E_{2\mathrm{H}}| \tag{25}$$

and it follows from Eqs. (15) to (18) that for very good basis expansions the value of $|\delta E_{\mathrm{tot}}|$ is lower for mixed basis computations than for uniform ones. For actual basis expansions, Eq. (22) does not hold exactly, but in all cases studied the relation

$$|\delta E_{1\mathrm{H}}/\delta E_{2\mathrm{H}}| > 2 \tag{26}$$

is fulfilled (the lowest value being $|\delta E_{1\mathrm{H}}/\delta E_{2\mathrm{H}}| \approx 2.8$) with the consequence that the unequality (19) and the statements following thereof are true even here.

Besides the energy shift $|\delta E_{\mathrm{tot}}|$, the changes of the virial coefficient $|\delta \mathit{Vir}|$ and $|\delta(E_1/E_2)|$ are much smaller for mixed bases than for uniform ones. Using uniform bases, the new scaling of the shortened basis causes changes $\delta \mathit{Vir}$ which are of the same order of magnitude as $|\delta E_{\mathrm{tot}}/E_{\mathrm{tot}}|$. With mixed bases $\delta \mathit{Vir}$ is smaller by about one power of ten. The slight electron shift induced by the change of basis takes place in such a way that the variation of kinetic energy δT_{p} nearly compensates the decrease of two-electron energy.

As conclusion for large molecules which require a shortened basis we suppose only those bases to yield reasonable results which fulfill the afore mentioned criterions. For those bases mixed calculations are recommendable because then E_{tot} as well as Vir will show less deviations from the original values than with uniform bases.

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