Gaussian Expansions of Minimal STO Basis for Calculations in Molecular Quantum Mechanics

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By means of minimal basis SCF calculations for HF, H_2O, NH_3 and CH_4 different expansions of Slater orbitals (STO) in terms of Gaussian orbitals (GTO) are tested in order to find an appropriate compromise between sufficient accuracy of the results and reasonable computing times. The least squares fit of the GTO expansion to STO does not appear to have any advantages over the expansion based on a variational procedure. It turns out that for hydrogens an expansion of the $1s$ orbital in terms of three GTO is quite sufficient, whereas for first row atoms an expansion of the $1s$ orbital in terms of three to five GTO, of the $2s$ orbital in terms of two GTO and of the $2p$ orbitals in terms of three GTO seems to be adequate.

An Hand von SCF-Rechnungen mit minimaler Basis für die Moleküle HF, H_2O, NH_3 und CH_4 wurden verschiedene Entwicklungen von Slater-Orbitalen (STO) nach Gauß-Orbitalen (GTO) getestet, um einen geeigneten Kompromiß zwischen ausreichender Genauigkeit der Ergebnisse und vertretbaren Rechenzeiten zu finden. Es zeigt sich, daß die Entwicklung der STO nach GTO mit Hilfe der Methode der kleinsten Fehlerquadrate keine Vorteile gegenüber der auf einem Variationsverfahren basierenden Entwicklung aufweist. Für H-Atome erweist sich eine Entwicklung des $1s$-Orbitals nach drei GTO als ausreichend, für Atome der 1. Periode erscheint eine Entwicklung des $1s$-Orbitals nach drei bis fünf GTO, des $2s$-Orbitals nach zwei GTO und der $2p$-Orbitale nach drei GTO als geeignet.

En vue de trouver un compromis approprié entre la précision et la durée des calculs, différents développements des orbitales de Slater (STO) en termes d'orbitales gaussiennes (GTO) sont testés au moyen de calculs SCF en bases minimales pour HF, H_2O, NH_3 et CH_4. L'ajustement par les moindres carrés du développement des STO en GTO ne présente apparemment d'avantages sur le développement fondé sur un procédé variationnel. Il apparaît que pour l'hydrogène un développement de l'orbitale $1s$ en fonction de trois gaussiennes est largement suffisant, alors que pour les atomes de la première rangée il semble nécessaire de développer l'orbitale $1s$ en 3 à 5 GTO, l'orbitale $2s$ en 2 GTO et les orbitales $2p$ en 3 GTO.

Introduction

Self-consistent group function (SCGF) calculations based on the separated-pair approximation have proved of great value in discussing chemical problems, particularly in the most simple form which is characterized by the use of a minimal set of basis orbitals [1]. But difficulties in the systematic determination of all molecular integrals will make the use of Slater-type orbitals (STO) prohibitive for large molecules of general geometry until considerably more effective programmes for the evaluation of many-center integrals are developed than those currently available. During the last few years Gaussian-type orbitals (GTO), originally introduced into quantum chemical calculations by Boys [2] and McWeeny [3], have proved successful in molecular calculations (cf. [4, 5]), as the need to use larger basis sets is more than compensated by the ease with which molecular integrals over GTO can be calculated.

The simplicity of minimal basis molecular calculations may be preserved in spite of the slow convergence of GTO-calculations through the use of a minimal basis set of contracted Gaussians (contracted GTO), i.e. linear combinations of Gaussian-type orbitals, as first suggested by Foster and Boys [6], and more recently by various authors [7]. The simulation of atomic Hartree-Fock-orbitals [8, 9] and of the double zeta STO basis [10] has been studied in detail, and contracted GTO bases are being used extensively (cf. [4, 10–12]). The present paper gives the results of Roothaan SCF calculations on the methane and the water molecule with different minimal basis sets of contracted GTO. These calculations were undertaken in order to numerically compare two different expansion methods discussed by Huzinaga [8] and by O-ohata, Taketa, and Huzinaga [13], and in order to find an appropriate compromise between sufficient accuracy and reasonable computing time, i.e. in order to determine a set of contracted GTO suitable for SCF and SCGF calculations [1] on large molecules.

Gaussian Expansion of Slater Orbitals

The GTO $\eta_{n'lm}$ used in the present paper are defined as

$$\eta_{n'lm}(\zeta', r) = N_{n'}(\zeta') \, r^{n'-1} \, \exp(-\zeta' r^2) \, Y_{lm}(\theta, \varphi), \tag{1}$$

where $N_{n'}(\zeta')$ is an appropriate normalizing factor [8]. The approximate expansion $\tilde{\varphi}_{nlm}(\zeta, r)$ of an STO $\varphi_{nlm}(\zeta, r)$ in terms of K of these GTO is generally expressed as

$$\tilde{\varphi}_{nlm}(\zeta, r) = \sum_{i=1}^{K} c_i \eta_{n'lm}(\zeta_i', r), \tag{2}$$

where the orbitals on both sides of this equation should have the same angular dependence, i.e. only η of the same l and m are included in the contraction given in (2). The prime is used to distinguish the GTO label n' and orbital exponent ζ' from the corresponding STO quantities. Furthermore, if one sets

$$\zeta_i' = \zeta^2 \alpha_i, \tag{3}$$

the exponent parameters α_i are, for a particular expansion, independent of the value of ζ [8, 13]. As shown by Huzinaga [8] all s-type STO are best expanded in terms of Gaussian $1s$-orbitals ($n' = 1$), p-type STO are best expanded in terms of $2p$-GTO ($n' = 2$) and d-type STO in terms of $3d$-GTO ($n' = 3$). Thus for $1s$, $2s$ and $2p$ orbitals (to which we will restrict ourselves with minimal basis calculations on molecules composed of first row atoms and hydrogen in mind) we have explicitly

$$\tilde{\varphi}_{1s}(\zeta, r) = \sum_{i}^{K} c_i^{(1s)} \eta_{1s}(\zeta^2 \alpha_i^{(1s)}, r),$$

$$\tilde{\varphi}_{2s}(\zeta, r) = \sum_{i}^{K} c_i^{(2s)} \eta_{1s}(\zeta^2 \alpha_i^{(2s)}, r), \tag{4}$$

$$\tilde{\varphi}_{2p}(\zeta, r) = \sum_{i}^{K} c_i^{(2p)} \eta_{2p}(\zeta^2 \alpha_i^{(2p)}, r),$$

Table 1. *Coefficients and exponent parameters for Gaussian expansion of Slater orbitals (method I)*

K	$\alpha_i^{(1s)}$	$c_i^{(1s)}$	K	$\alpha_i^{(2s)}$	$c_i^{(2s)}$
2	0.2015264	0.82122535	2	0.1059647	1.00725532
	1.332467	0.27440872		4.171148	-0.04842184
3	0.1513626	0.64762487	3	0.0553757	0.38684504
	0.6811910	0.40792769		0.1426136	0.65943056
	4.499779	0.07048736		3.780114	-0.05460844

K	$\alpha_i^{(2p)}$	$c_i^{(2p)}$
2	0.1295680	0.78540458
	0.5571040	0.32565205
3	0.0987360	0.57859970
	0.3193200	0.47405684
	1.348288	0.09204572

K	$\alpha_i^{(1s)}$	$c_i^{(1s)}$
4	0.1219455	0.50108255
	0.4445003	0.47831666
	1.961863	0.13798736
	13.00775	0.01968788
5	0.1013090	0.37602145
	0.3211440	0.50821418
	1.146800	0.20571931
	5.057960	0.04575350
	33.64441	0.00611802

where

$$\eta_{1s}(\zeta^2\alpha_i, r) = [8(\zeta^2\alpha_i)^3/\pi^3]\exp(-\zeta^2\alpha_i r^2) \tag{5}$$

and

$$\eta_{2p}(\zeta^2\alpha_i, r) = [128(\zeta^2\alpha_i)^5/\pi^3]\, r\exp(-\zeta^2\alpha_i r^2)\begin{cases}\cos\theta\\ \sin\theta\cos\varphi.\\ \sin\theta\sin\varphi\end{cases}$$

Optimum values for the parameters c_i and α_i may be obtained by two different methods. *Method I is based on a variational procedure* due to McWeeny [3], and has been used and described in detail by Huzinaga [8]. In this method the energy of the GTO expansion for an appropriate Hamiltonian whose eigenfunctions are the corresponding STO is minimized with respect to the α_i and c_i. As Huzinaga gives the c_i only to five decimal figures and as there are some misprints in his tables some of his values have been recalculated and are given in Table 1.

Method II is a least squares fit of the Gaussian expansion to the STO and is based on a minimization of the integral

$$\varepsilon = \int [\varphi_{nlm}(\zeta, r) - \sum_i^K c_i\eta_{n'lm}(\zeta^2\alpha_i, r)]^2\,d\tau \tag{6}$$

with respect to the α_i and c_i. This procedure was suggested by O-ohata, Taketa, and Huzinaga [13], who gave values of c_i and α_i for $K = 4, 6, 8$ and 10, whereas Hehre, Stewart, and Pople [14] determined the c_i and α_i for $K = 3, 4,$ and 5. In the present paper we use the values given in Table 1 of Ref. [14].

Method of Computation

LCAO-MO-SCF calculations were performed for HF, H_2O, NH_3 and CH_4 with equilibrium ground state geometries as given in Table 2, using different minimal basis sets of contracted GTO as described in the previous section, i.e.

Table 2. *Cartesian coordinates used for SCF calculations (in bohrs)* [a]

Molecule	Atom	x	y	z
HF	H	1.733120	0.0	0.0
H_2O	H_1	1.436208	0.0	1.102041
	H_2	-1.436208	0.0	1.102041
NH_3	H_1	1.722045	0.0	-0.721190
	H_2	-0.866023	1.534640	-0.721190
	H_3	-0.866023	-1.534640	-0.721190
CH_4	H_1	1.192517	1.192517	1.192517
	H_2	1.192517	-1.192517	-1.192517
	H_3	-1.192517	1.192517	-1.192517
	H_4	-1.192517	-1.192517	1.192517

[a] The heavy atom is at the origin of the coordinate system. 1 bohr $= 0.52917$ Å.

STO were expanded in terms of $K = 2$ to $K = 5$ Gaussians, by means of the parameters of method I as well as those of method II. The orbital exponents ζ of the STO for first row atoms are the optimum values ($\zeta_C = 5.6727, 1.6083, 1.5679$; $\zeta_N = 6.6651$, $1.9237, 1.9170$; $\zeta_O = 7.6579, 2.2458, 2.2266$; $\zeta_F = 8.6501, 2.5638, 2.5500$ for the $1s$, $2s$ and $2p$ AO respectively) given by Clementi and Raimondi [15], whereas for the hydrogen atom $\zeta_H = 1.00$ was used except in those cases where ζ_H was optimized (cf. Table 8 for optimum ζ_H-values).

The programme used for these calculations is based on the POLYATOM programme system QCPE 47 [16] and is written in FORTRAN IV and MAP for the IBM 7040/32 K of the computer centre Göttingen. It forms part of a general programme system MOLCAL for SCF and SCGF calculations on polyatomic molecules of general geometry, which will shortly be made available through QCPE. By far the most time-consuming step in these calculations is the evaluation of all molecular integrals which follows the general philosophy of the POLYATOM programme, i.e. first a minimum list of integrals required to be calculated is set up from specifications of the symmetry properties of the basis orbitals; the one and two-electron integrals over contracted GTO are then evaluated as specified by this list, each integral being expanded in terms of integrals over GTO, e.g.

$$(\tilde{\varphi}_i \tilde{\varphi}_j \mid \tilde{\varphi}_k \tilde{\varphi}_l) = \sum_{\kappa}^{K_i} \sum_{\lambda}^{K_j} \sum_{\mu}^{K_k} \sum_{\nu}^{K_l} c_\kappa^{(i)} c_\lambda^{(j)} c_\mu^{(k)} c_\nu^{(l)} (\eta_\kappa \eta_\lambda \mid \eta_\mu \eta_\nu). \tag{7}$$

In carrying out this expansion care is taken of the identity

$$(\kappa\lambda \mid \mu\nu) = (\kappa\lambda \mid \nu\mu) = (\lambda\kappa \mid \mu\nu) = (\lambda\kappa \mid \nu\mu) = (\mu\nu \mid \kappa\lambda) = (\nu\mu \mid \kappa\lambda) = (\mu\nu \mid \lambda\kappa) = (\nu\mu \mid \lambda\kappa)$$

in order to reduce the computing time. Although some of the integrals $(\eta_\kappa \eta_\lambda \mid \eta_\mu \eta_\nu)$ over GTO are calculated more than once this procedure is considerably faster than the alternative way which consists in first calculating all integrals over GTO and then transforming them into integrals over contracted GTO. This is mainly so because even for small molecules and relatively small expansions of the basis orbitals the core storage cannot hold all the integrals over GTO. Computer times

necessary for the evaluation of all integrals over contracted GTO are given together with the results in Table 5, 6, and 7. The time required for setting up the minimum list of integrals and for carrying out the SCF calculations is in the order of 10 sec and 45 sec respectively for all molecules considered in the present paper.

Results and Discussion

Results of SCF calculations with different expansions of minimal sets of basis orbitals are reported in Tables 5–9. Tables 5–8 give the calculated total ground state energy E_0, the kinetic energy E_k and the binding energy D (evaluated as difference between the molecular energy E_0 and the energy of the constituent atoms calculated with the same basis orbitals and listed in Tables 3 and 4), together with the orbital energies and the gross atomic orbital populations and overlap populations as defined by Mulliken [17]. Different expansions are denoted by $X(K_{1s}, K_{2s}, K_{2p})$ (e.g. C (5, 2, 3)) and $H(K_{1s})$ respectively, where X is the first row atom under consideration, H the hydrogen atom, and K_{1s}, K_{2s} and K_{2p} are the numbers of GTO in the expansions Eq. (4) of the $1s$, $2s$ and $2p$ orbitals respectively. If the number specifying the uncontracted functions are given in round brackets while the contracted basis set is in square brackets, the given examples read:
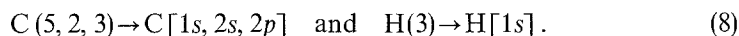
$$C (5, 2, 3) \rightarrow C [1s, 2s, 2p] \quad \text{and} \quad H(3) \rightarrow H[1s] . \tag{8}$$

Table 3. *Total energies (hartrees) of the C, N, O and F atoms obtained by different Gaussian expansions according to method I and method II*

	C (^3P)		N (^4S)	O (^3P)		F (^2P)
	Method I	Method II	Method I	Method I	Method II	Method I
X (3, 2, 3)	− 37.367697	—	− 53.906688	− 74.046740	—	− 98.149808
X (3, 3, 3)	− 37.392727	− 37.227602	− 53.944093	− 74.099084	− 73.797425	− 98.361395
X (4, 2, 2)	− 37.473047	—	—	− 74.100536	—	—
X (4, 2, 3)	− 37.526822	—	—	− 74.330829	—	—
X (5, 2, 2)	− 37.509377	—	—	− 74.165918	—	—
X (5, 2, 3)	− 37.563140	—	− 54.173624	− 74.396161	—	− 98.734973
X (5, 3, 3)	− 37.588674	− 37.570919	− 54.211754	− 74.449545	− 74.409239	− 98.806058

Table 4. *Total energies (hartrees) of the H (^2S) atom obtained by different Gaussian expansions*

	ζ_H	E_0
H (3)	1.0000	− 0.496980 (− 0.494908) [a]
H (4)	1.0000	− 0.499278
H (3)	1.2019	− 0.476722
H (3)	1.2457	− 0.466979
H (3)	1.2462	− 0.466856
H (3)	1.2473	− 0.466587
H (3)	1.2542	− 0.464867

[a] Value in brackets according to method II, all other values according to method I.

Table 5. Comparison of SCF results of H_2O and CH_4 for expansion of basis orbitals according to method I and method II [a]

| | | H₂O | | | | | CH₄ | | | |
| | | O(3,3,3), H(3) | | O(5,3,3), H(3) | | | C(3,3,3), H(3) | | C(5,3,3), H(3) | |
		Method I	Method II	Method I	Method II		Method I	Method II	Method I	Method II
Total energy	E_0	−75.2255	−74.9086	−75.5709	−75.5180	E_0	−39.8124	−39.6319	−40.0009	−39.9674
Virial coeff.	$(E_0 - E_k)/E_k$	− 2.0110	− 2.0066	− 2.0030	− 2.0034	$(E_0 - E_k)/E_k$	− 2.0389	− 2.0304	− 2.0285	− 2.0259
Binding energy	D	0.1325	0.1214	0.1274	0.1189	D	0.4318	0.4247	0.4243	0.4169
Orbital energies	$1a_1$	−20.4338	−20.2971	−20.5901	−20.5784	$1a_1$	−11.3082	−11.2119	−11.3885	−11.3641
	$2a_1$	− 1.3056	− 1.3067	− 1.3082	− 1.3203	$2a_1$	− 0.9711	− 0.9658	− 0.9718	− 0.9712
	$1b_1$	− 0.6422	− 0.6403	− 0.6426	− 0.6396	$1t_2$	− 0.5757	− 0.5717	− 0.5756	− 0.5705
	$3a_1$	− 0.4781	− 0.4761	− 0.4789	− 0.4777	$3a_1$	0.4643	0.4386	0.4631	0.4325
	$1b_2$	− 0.4276	− 0.4278	− 0.4284	− 0.4277	$2t_2$	0.4855	0.5013	0.4856	0.5025
	$4a_1$	0.4004	0.3956	0.3989	0.3922					
	$2b_1$	0.5638	0.5843	0.5630	0.5845					
Populations	H	0.8022	0.8021	0.7997	0.8006	H	0.8323	0.8319	0.8307	0.8289
	O(1s)	1.9967	1.9979	1.9984	1.9987	C(1s)	1.9901	1.9940	1.9953	1.9962
	O(2s)	1.8770	1.8752	1.8793	1.8868	C(2s)	1.3714	1.3808	1.3717	1.3974
	O(2px)	1.0395	1.0443	1.0413	1.0443	C(2p)	1.1031	1.0992	1.1034	1.0970
	O(2py)	2.0	2.0	2.0	2.0					
	O(2pz)	1.4825	1.4784	1.4815	1.4690					
	n(O–H)	0.4407	0.4521	0.4380	0.4404	n(CH)	0.7802	0.7826	0.7824	0.7809
Dipole moment	μ	1.64	1.59	1.64	1.56					
Integral evaluation		9 min		13 min			6.6 min		9.1 min	

[a] All energies in hartrees (1 hartree = 27.2098 eV), dipole moment in debye.

The data in Tables 5–9 are self-explanatory, thus only a few remarks will be added. Table 5 gives a comparison of the results for H_2O and CH_4 with an expansion of the basis orbitals according to method I and method II. From these results it is seen that method I gives invariably lower total energies E_0 than method II, especially so for an expansion of the $1s$ orbitals in terms of only 3 GTO.

Apparently it is mainly the $1s$ orbitals which turn out to be worse in method II than in method I, as may be seen from the orbital energies. Results of the population analysis are very similar for the calculations according to both methods, but method I gives not only lower total energies but also better binding energies D. Thus, although method II was introduced because it was thought to be much better suited for molecular calculations than method I [13], it does not seem to have any advantages. In the following we will therefore concentrate on method I, i.e. on the expansion of STO in terms of GTO with expansion coefficients and exponent parameters determined by a variational procedure.

In Table 6 results for H_2O for different expansions of the basis orbitals are collected. As expected the total ground state energy E_0 becomes lower as the number of GTO is increased, but it should be noted that increasing K_{2s} has a neglibible effect compared with increasing K_{1s} and K_{2p}; thus O (3, 3, 3) and O (4, 2, 3), which both correspond to 15 GTO on the oxygen, give total energies $E_0 = -75.2255$ and $E_0 = -75.4746$ hartrees respectively. There is no similar regularity in the calculated binding energies D, the highest values are obtained for O (4, 2, 2) and O (5, 2, 2), the lowest values for O (5, 3, 3) and O (3, 3, 3). According to the calculated dipole moment and the gross atomic population N(H) of the

Table 6. SCF *results of* H_2O *for different expansions of basis orbitals according to method I* (H(3) *in all cases)*[a]

		O (3, 2, 3)	O (4, 2, 2)	O (4, 2, 3)	O (5, 2, 2)	O(5,2,3)
Total energy	E_0	-75.1934	-75.2549	-75.4746	-75.3194	-75.5391
Virial coeff.	$(E_0 - E_k)/E_k$	-2.0136	-2.0082	-2.0086	-2.0057	-2.0061
Binding energy	D	0.1527	0.1604	0.1499	0.1595	0.1489
Orbital energies	$1a_1$	-20.4517	-20.6716	-20.5830	-20.6993	-20.6105
	$2a_1$	-1.2960	-1.3154	-1.2973	-1.3158	-1.2976
	$1b_1$	-0.6407	-0.6323	-0.6410	-0.6324	-0.6412
	$3a_1$	-0.4692	-0.4486	-0.4697	-0.4489	-0.4499
	$1b_2$	-0.4255	-0.3925	-0.4261	-0.3928	-0.4263
	$4a_1$	0.3861	0.3973	0.3852	0.3969	0.3848
	$2b_1$	0.5659	0.5790	0.5653	0.5788	0.5651
Populations	H	0.8182	0.8718	0.8165	0.8712	0.8159
	O $(1s)$	1.9970	1.9983	1.9981	1.9988	1.9986
	O $(2s)$	1.8109	1.8453	1.8118	1.8456	1.8121
	O $(2px)$	1.0413	0.9899	1.0426	0.9903	1.0431
	O $(2py)$	2.0	2.0	2.0	2.0	2.0
	O $(2pz)$	1.5144	1.4229	1.5146	1.4228	1.5144
	n (OH)	0.5125	0.4443	0.5119	0.4439	0.5115
Dipole moment	μ	1.67	1.40	1.68	1.40	1.68
Integral evaluation		7.4 min	5.8 min	9 min	6.9 min	10.9 min

[a] All energies in hartrees, dipole moment in debye.

hydrogens the results may be divided into two groups: for O (4, 2, 2) and O (5, 2, 2) $\mu = 1.40\,D$ and N(H) $= 0.87$, whereas for all other basis sets $\mu = 1.64\,D$ and N(H) $= 0.80$–0.82. Inspection of the overlap population n(OH) results in a different grouping: if $K_{2s} = K_{2p}$, n(OH) is approximately 0.44, whereas for $K_{2s} < K_{2p}$ one finds n(OH) ≈ 0.51. The orbital energies do not vary significantly, except for the energy of the lowest orbital $(1a_1)$ which naturally depends on K_{1s}.

The results for CH_4, which are collected in Table 7, show a very similar behaviour, but here C (3, 3, 3) and C (5, 3, 3) lead to higher total energies E_0 than C (3, 2, 3) and C (5, 2, 3) respectively. Again, for C (4, 2, 2) and C (5, 2, 2) the gross atomic population N(H) $= 0.87$ is higher than for all other basis sets for which N(H) ≈ 0.84; the highest value of the binding energy D is obtained for C (5, 2, 2), the lowest value for C (5, 3, 3). In Table 5 a methane calculation with approximate atomic Hartree-Fock orbitals as given by Huzinaga [8] is included under the heading C (9, 5, 5). It is seen that the results of this calculation are fairly well reproduced by the GTO expansions, particularly so by C (4, 2, 3) and C (5, 2, 3), apart from the fact that the Hartree-Fock orbitals lead to rather low values of the binding energy and the atomic gross population of the hydrogens. Also shown are the results of calculations for C (4, 2, 3) and C (5, 2, 3) with an expansion of the hydrogen 1s orbital in terms of 4 GTO. Such an expansion H (4) results in a considerable increase in computer time for the evaluation of the molecular integrals but only a very slight improvement of the total energy is achieved and all other quantities are hardly affected, in comparison with the expansion H (3).

As is well known $\zeta_H = 1.0$ for the orbital exponent of the hydrogen 1s orbital is not particularly suited for molecular calculations. Optimization of the ζ_H-value leads to an appreciable improvement of the total energy as well as the binding energy, as can be seen from the data of Table 8. (Binding energies in Table 8 were evaluated as differences between the molecular energies and the energies of the constituent atoms calculated with free atom orbital exponents, i.e. $\zeta_H = 1.0$.) This increase in binding energy while going from $\zeta_H = 1.0$ to optimized ζ_H values is paralleled by a considerable decrease in the gross atomic population on the hydrogens, which leads to an appreciable increase of the calculated dipole moment. Inspection of the virial coefficient $(E_0 - E_k)/E_k$, particularly for H_2O, shows that the oxygen orbital exponents may not be far from optimum values. Thus the calculated charge distribution can be expected to be fairly realistic, as is confirmed by a comparison of the calculated dipole moment $\mu = 1.84$ and $\mu = 1.87$ debye for O (5, 2, 3) and O (5, 3, 3) respectively with the experimental value $\mu = 1.846$ debye [18]. But it should be noted that even for optimized ζ_H values there appear to be differences in the calculated charge distributions, if different expansions of the basis orbitals are used, as may be seen e.g. from the methane data for C (4, 2, 2) and C (4, 2, 3). It remains to be shown whether these differences disappear if the carbon orbital exponents are also optimized, or whether in fact $K_{2p} = 2$ is not sufficient in order to give realistic results.

In Table 9 total ground state energies E_0 for an expansion of the 2s orbital in terms of two and three GTO ($K_{2s} = 2$ or 3) are given for HF, H_2O, NH_3 and CH_4. It turns out that $K_{2s} = 3$ leads for HF to E_0 values lower by an amount $\Delta E = 0.06$ hartree than $K_{2s} = 2$, whereas $K_{2s} = 3$ gives for CH_4 a slightly higher E_0 than $K_{2s} = 2$, H_2O and NH_3 lying inbetween these two cases. Thus in molecules

Table 7. SCF results of CH_4 for different expansions of basis orbitals according to method I[a]

		C(3, 2, 3), H(3)	C(4, 2, 2), H(3)	C(4, 2, 3), H(3)	C(4, 2, 3), H(4)	C(5, 2, 2), H(3)	C(5, 2, 3), H(3)	C(5, 2, 3), H(4)	C(9, 5, 5), H(3)[b]
Total energy	E_0	−39.8141	−39.9192	−39.9692	−39.9770	−39.9642	−40.0043	−40.0126	−40.0402
Virial coeff.	$(E_0 - E_k)/E_k$	− 2.0384	− 2.0316	− 2.0323	− 2.0317	− 2.0288	− 2.0293	− 2.0287	− 2.0205
Binding energy	D	0.4585	0.4582	0.4545	0.4531	0.4670	0.4532	0.4524	0.3670
Orbital energies	$1a_1$	−11.3097	−11.4160	−11.3793	−11.3790	−11.4298	−11.3931	−11.3928	−11.3866
	$2a_1$	− 0.9710	− 0.9742	− 0.9713	− 0.9702	− 0.9742	− 0.9731	− 0.9702	− 1.0062
	$1t_2$	− 0.5724	− 0.5642	− 0.5723	− 0.5642	− 0.5732	− 0.5732	− 0.5732	− 0.6044
	$3a_1$	0.4086	0.4077	0.4081	0.3916	0.4075	0.4079	0.3912	0.4550
	$2t_2$	0.4891	0.4937	0.4890	0.4906	0.4937	0.4890	0.4906	0.4762
Populations	H	0.8430	0.8694	0.8419	0.8459	0.8698	0.8416	0.8455	0.7690
	C (1s)	1.9918	1.9949	1.9947	1.9949	1.9963	1.9961	1.9962	2.0004
	C (2s)	1.3235	1.3392	1.3234	1.3318	1.3388	1.3230	1.3315	1.3668
	C (2p)	1.1042	1.0628	1.1048	1.0966	1.0629	1.1049	1.0967	1.1857
	n (CH)	0.7852	0.7821	0.7865	0.7861	0.7826	0.7870	0.7866	0.7922
Integral evaluation		5.7 min	4.9 min	6.7 min	11.0 min	5.9 min	7.8 min	12.7 min	53.6 min

[a] All energies in hartrees.
[b] Approximate atomic Hartree-Fock-orbitals, as given by Huzinaga [8].

Table 8. SCF results for H_2O and CH_4 with optimized orbital exponents ζ_H [a]

	H_2O			CH_4		
	$O(5,2,3)$ $\zeta_H = 1.2473$	$O(5,3,3)$ $\zeta_H = 1.2542$		$C(4,2,2)$ $\zeta_H = 1.2019$	$C(4,2,3)$ $\zeta_H = 1.2462$	$C(5,2,3)$ $\zeta_H = 1.2457$
Total energy	-75.5792	-75.6124	E_0	-39.9565	-40.0239	-40.0590
Virial coeff.	-2.0038	-2.0013	$(E_0 - E_k)/E_k$	-2.0212	-2.0197	-2.0169
Binding energy	0.1891	0.1689	D	0.4955	0.5092	0.5079
Orbital energies	-20.5730	-20.5521	$1a_1$	-11.3514	-11.2931	-11.3073
	-1.2672	-1.2778	$2a_1$	-0.9420	-0.9307	-0.9308
	-0.6196	-0.6198	$1t_2$	-0.5306	-0.5320	-0.5322
	-0.4502	-0.4573	$2t_2$	0.6378	0.6697	0.6693
	-0.3930	-0.3930	$3a_1$	0.6585	0.7180	0.7172
	0.5888	0.6200				
	0.7213	0.7242				
Populations	0.8110	0.7958	H	0.8612	0.8275	0.8273
	1.9985	1.9983	$C(1s)$	1.9947	1.9946	1.9960
	1.7956	1.8389	$C(2s)$	1.2863	1.2812	1.2805
	1.0918	1.0895	$C(2p)$	1.0914	1.1381	1.1381
	2.0	2.0				
	1.4921	1.4816				
	0.5605	0.5219	$n(CH)$	0.7845	0.7805	0.7811
Dipole moment	1.84	1.87	μ	—	—	—

Populations (left labels): H, $O(1s)$, $O(2s)$, $O(2px)$, $O(2py)$, $O(2pz)$, $n(OH)$

[a] All energies in hartrees, dipole moment in debye.

Table 9. *Comparison of total energies E_0 for an expansion of the 2s orbital in terms of 2 and 3 GTO, H (3) in all cases* [a]

	E_0 X (3, 2, 3)	E_0 X (3, 3, 3)	ΔE	E_0 X (5, 2, 3)	E_0 X (5, 3, 3)	ΔE
HF	− 98.8543	− 98.9133	0.059	− 99.2952	− 99.3548	0.060
H_2O	− 75.1934	− 75.2255	0.032	− 75.5391	− 75.5709	0.032
NH_3	− 55.6357	− 55.6462	0.010	− 55.8979	− 55.9072	0.009
CH_4	− 39.8141	− 39.8124	−0.002	− 40.0043	− 40.0009	−0.003

[a] All energies in hartrees.

Table 10. *Total energies (hartrees) for the CH_4, NH_3, H_2O and HF molecules*

	CH_4	NH_3	H_2O	HF
Present calculations	− 40.0590	− 55.9072	− 75.6124	− 99.3548
Min. basis of STO	− 40.0606 [a]	− 56.0960 [b]	− 75.6617 [c]	− 99.4786 [d]
Extended basis set	− 40.1983 [e]	− 56.2268 [f]	− 76.0421 [g]	− 100.0708 [h]
Experimental [i]	− 40.526	− 56.605	− 76.485	− 100.560

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[h] Cade, P. E., Huo, W. M.: J. chem. Physics 47, 614 (1967).
[i] from Ref. [4].

with no or only one lone pair of electrons $K_{2s} = 3$ appears to have no advantage over $K_{2s} = 2$.

Finally, in Table 10 experimental values of the total ground state energies for CH_4, NH_3, H_2O and HF are collected together with results of calculations with minimal basis sets of STO and of previous best calculations. It is seen that the present results compare rather well with those based on a minimal STO set, although it should be kept in mind that the aim of the present work was not to compute absolute energies as accurately as possible, but rather to obtain minimal basis sets which make it possible to carry out ab initio calculations on sufficiently large molecules with reasonable computing times.

In conclusion we may summarize our results as follows.

1. The least squares fit of an Gaussian expansion to STO (method II) does not appear to have any advantage over the Gaussian expansion based on a variational procedure (method I).

2. An expansion of the hydrogen 1s orbital in terms of three GTO seems to be sufficient in most cases.

3. For the 2p orbitals of first row atoms an expansion in terms of three GTO is recommended.

4. For the 2s orbital of first row atoms an expansion in terms of two GTO seems to be sufficient, perhaps with the exception of atoms which have two or more lone pairs of electrons.

5. Depending on the desired accuracy for the total energy, an expansion of the 1s orbital of first row atoms in terms of three, four, five or even more GTO can be used, as the number of GTO in this expansion effects only the total energies and the energies of the lowest molecular orbitals.

Overall, we may conclude that the expansion of STO in terms of a small number of GTO is very well suited for minimal basis molecular calculations. X (4, 2, 3) or X (5, 2, 3) for first row atoms X represents an appropriate compromise between sufficient accuracy and reasonable computing time. Here again, the advantage of X (4, 2, 3) over X (3, 3, 3), both corresponding to 15 GTO on atom X, should be emphasized.

The expansion X (5, 2, 3) together with H (3) has been used in quite a number of minimum basis SCF and SCGF calculations on larger molecules; results of these calculations will be presented in forthcoming papers.

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