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Merged Gaussian Lobe Basis SCFMO Calculations

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Some merged basis set calculations are described in which the magnitude of the computational labour is greatly reduced by using smaller Gaussian lobe bases for computing the 3- and 4-centre two-electron integrals, the full basis being employed for all one-electron and one-and two-centre two-electron integrals. The several merged bases that have been investigated have all performed exceedingly well when total energy and some one-electron operator expectation values are used as criteria.

The performance with respect to dipole moment is not quite as impressive as for the other expectation values.

If present results can be taken as a general guide then it is questionable whether large Gaussian basis calculations that do not make use of the merging procedure have any advantage to offset the greater computing cost involved.

Es wird über eine Methode berichtet, die Computerzeit bei Rechnungen mit Gaußfunktionbasissätzen wesentlich zu verkürzen, in dem man kleinere Sätze von Gaußfunktionen für die 3- und 4-Zentren-Zweielektronenintegrale verwendet, dagegen die gesamte Basis für alle Einelektronen- und Ein- und Zweizentren-Zweielektronenintegrale.

Die untersuchten Basissätze dieser Art gestatten eine gute Berechnung der Gesamtenergie und der Erwartungswerte einiger Elektronenoperatoren. Allerdings tritt eine größere Abweichung bei der Berechnung des Erwartungswertes für das Dipolmoment auf. Wenn sich die dargelegten Resultate als allgemeingültig erweisen, ist es fraglich, ob Berechnungen mit großen Gaußfunktionsbasissätzen, die ohne diese „Verschmelzungs"-Prozedur durchgeführt werden, einen Vorteil bieten, der die größeren Computerkosten rechtfertigt.

Description de calculs avec des bases gaussiennes tronquées où le temps de calcul est réduit en n'utilisant que des bases plus petites pour les intégrales bi-électroniques à trois et quatre centres. Les différentes bases tronquées employées donnent de bons résultats lorsque l'énergie et les valeurs moyennes de certains opérateurs monoélectroniques sont pris comme critères. Les résultats obtenus pour le moment dipolaire sont moins bons.

Si l'on peut prendre les résultats présentés comme guide on peut se demander si l'emploi de grandes bases non tronquées présente un avantage réel vu le prix du calcul.

Introduction

In recent years almost all "ab intio" calculations on polyatomic molecules [1] have employed Gaussian function basis sets because the time-consuming two electron repulsion integrals reduce to simple analytical expressions with Gaussians [2]. It is well known that exponentials are solutions to the central field problem and it is therefore not surprising that many more Gaussians than exponentials must be used to achieve comparable accuracy. Because of the large number of Gaussians which must be used, it has also been found necessary to "group" the basis functions so that fewer parameters are left to vary in the SCF procedure.

Hence due to the large number of integrals that must be calculated, the initial speed advantage of Gaussians over exponentials is reduced.

It would seem that there are two alternatives available to reduce the time factor in "ab initio" calculations using Gaussian functions. Firstly, one could use a smaller number of Gaussians per group. This method has the advantage that there are fewer integrals to calculated and therefore the time is reduced, but it also means that all interactions, large and small, are being calculated with a less accurate basis set. The second alternative, which would seem more attractive, is to use a large basis set for the important interactions and a smaller set for the less important interactions.

The ideals incorporated in these two alternatives have been investigated by several workers [11–14] aiming to reduce the computational labour involved in *ab initio* MO calculations employing Slater type orbitals. Pople and coworkers [11, 12] have essentially used the first method in their gaussian expansion of Slater type orbitals technique. McWeeny, Palmieri and Cook [13, 14] have performed calculations in which they calculate all one electron integrals exactly using Slater type orbitals and normal "*C*" function techniques, and then use a small gaussian expansion to calculate *all* the repulsion integrals. Brown, Burden and Williams [10] have pointed out that this method unnecessarily approximates many repulsion integrals which are quite easily calculated using a Slater basis.

We have tested this second method by performing calculations employing large Gaussian lobe basis sets [3] for all one-electron and one-and two-centre two-electron integrals and a smaller lobe set for the three- and four-centre two-electron integrals. Thus the largest integrals are calculated quite accurately while the large number of smaller three- and four-centre repulsion integrals are calculated less accurately but with greater speed.

This paper outlines the small basis sets used and the application of this method to H_2O, NH_3 and CH_4.

Basis Sets

Lobe functions basis sets [3] have been used extensively over the last few years and indications are that they lead to quite adequate values for total energy [4], rotational barriers [5] and many one-electron properties [6]. The large basis sets employed in the present calculations were those reported by Whitten [3] which have been shown [7] to be very close to double zeta accuracy.

The small basis sets were obtained by least square fitting to the larger set using the Fletcher-Powell minimization procedure [8]. One-, two- and three-component fits were obtained or carbon, nitrogen, oxygen and hydrogen, and are listed, together with their overlap with the corresponding large group, in Table 1 and Table 2. If we represent a large basis set group function by ϕ_l and the corresponding small group function by ϕ_s where

$$\phi_l = \sum_i^N C_{il}\gamma_i$$

$$\phi_s = \sum_j^n C_{js}\gamma_j \qquad N > n$$

Table 1

Number of components in group	Carbon			Nitrogen			Oxygen		
	Exponent	Coefficient	Overlap	Exponent	Coefficient	Overlap	Exponent	Coefficient	Overlap
SS 1	252.4464	1.0000	0.980	345.6397	1.0000	0.980	469.0962	1.0000	0.979
IS 2	5.2959	0.7431	0.998	7.3284	0.7424	0.998	9.7325	0.7438	0.998
	29.2976	0.3546		40.2677	0.3548		53.4459	0.3530	
LS 2	0.3016	1.0143	0.993	0.4314	1.0139	0.993	0.5907	1.0134	0.992
	6.2346	−0.0583		8.9961	−0.0569		12.4582	−0.0552	
P 2	0.3609	7.4168 (0.10)	0.978	0.5311	6.0892 (0.10)	0.977	0.7104	5.2574 (0.10)	0.974
	2.7976	1.0827 (0.07)		4.1248	0.9227 (0.07)		5.6516	0.8110 (0.07)	
3	1.1250	2.0408 (0.10)	0.996	1.6504	1.7212 (0.10)	0.996	0.4140	5.2789 (0.10)	0.996
	0.2264	10.4953 (0.07)		0.3273	8.6404 (0.07)		2.1500	2.2385 (0.07)	
	7.1309	0.2213 (0.06)		10.1963	0.1977 (0.06)		13.5700	0.1856 (0.06)	

Numbers in brackets represent the distance (a. u.) of the lobe centres from the nucles.

Table 2

No. components	Hydrogen		
	Exponent	Coefficient	Overlap
2	0.5402	0.9268	0.989
	6.2604	0.1577	
3	0.3589	0.7563	0.998
	2.0558	0.3319	
	21.5927	0.0328	

and in the lobe representation for an S function

$$\gamma_i = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp(-\alpha_i r^2)$$

and for a P function

$$\gamma_i = N^{-1}\left(\frac{2\alpha_i}{\pi}\right)^{3/4} \{\exp(-\alpha_i r_1^2) - \exp(-\alpha_i r_2^2)\}$$

then the error in approximating ϕ_l by ϕ_s is given by

$$\Delta = \phi_l - \phi_s .$$

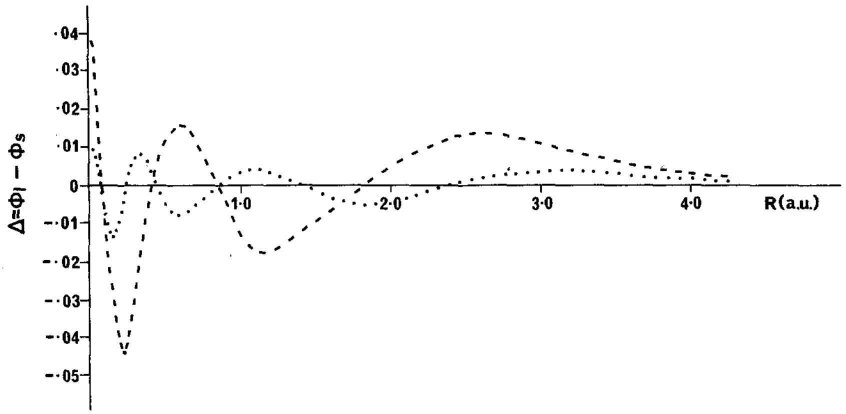


Fig. 1. Least square fits to a five component function for Hydrogen, --- two component fit, ···· three component fit, $\Delta = \Phi_l - \Phi_s$, Φ_l = large group function, Φ_s = small group function, R = distance from the nucleus

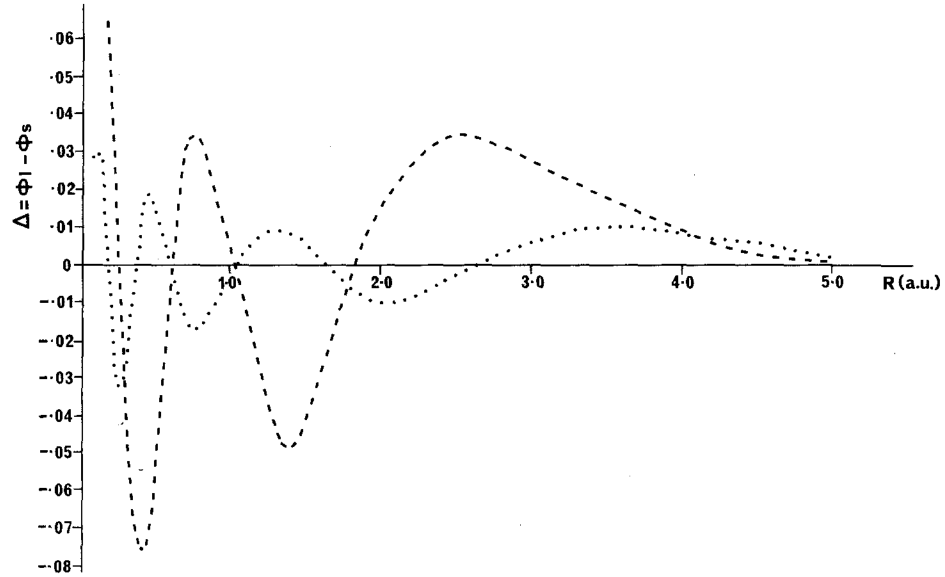


Fig. 2. Least square fits to a five component function for Oxygen. --- two component fit, ···· three component fit, $\Delta = \Phi_l - \Phi_s$, Φ_l = large group function, Φ_s = small group function, R = distance from the nucleus

One would expect that as n approaches N, Δ would be small in all regions of space. Fig. 1 shows the reduction in Δ at various distances from the nucleus for two- and three-component fits to the five-component lobe function for hydrogen [9] while Fig. 2 shows a similar reduction in Δ for two- and three-component fits to five-component P lobe functions for oxygen. In all cases the greatest deviation is experienced close to the nucleus and this, coupled with the fact that the large group functions are also in error in this region [3, 7], would indicate that these

Table 3. H_2O — *Orbital energies*

Molecular orbital	Basis set O (1222) H (3)	 O (1223) H (3)	 O (3435) H (5)
$1a_1$	−20.4787	−20.4423	−20.4579
$2a_1$	− 1.3410	− 1.3229	− 1.3216
$1b_2$	− 0.6940	− 0.6678	− 0.6809
$3a_1$	− 0.5492	− 0.5270	− 0.5379
$1b_1$	− 0.4928	− 0.4769	− 0.4844
E_{Tot}	−75.9947	−75.9587	−75.9747

All energies in atomic units.

Table 4. NH_3 — *Orbital energies*

Molecular orbital	Basis set N (1222) H (3)	 N (1223) H (3)	 N (3435) H (5)
$1a_1$	−15.4711	−15.4273	−15.4663
$2a_1$	− 1.1428	− 1.1209	− 1.1162
$1e$	− 0.6046	− 0.5737	− 0.6028
$3a_1$	− 0.3955	− 0.3751	− 0.4002
E_{Tot}	−56.1454	−56.0880	−56.1418

All energies in atomic units.

small sets will probably give a poor representation of one-centre integrals and any one-electron properties concerned with the nucleus (e.g. electric field gradient).

Following the notation of Whitten, our basis sets are composed of three *S*-type groups (one short range (SS), one intermediate range (IS) and one long range (LS)) and three *P*-type groups. The IS and LS groups correspond approximately to normal 1*s* and 2*s* atomic orbitals. The shorthand notation used to designate the large basis sets for first row atoms is (3 4 3 5) meaning a three-component SS group, a four-component IS group, a three-component LS group and a five-component *P* group are used.

In this preliminary work we report calculations using basis sets (1 2 2 2) and (1 2 2 3) on the heavy atoms and a three-component group for the hydrogen.

Discussion and Results

Orbital energies and total energies from calculations on H_2O, NH_3 and CH_4 employing the above small basis sets to approximate the 3- and 4-centre integrals, are recorded in Tables 3, 4 and 5. Tables 6, 7 and 8 record several one electron properties obtained from these calculations. For comparison purposes, the last column of each table contains the results from "exact" calculations employing Whitten's large basis sets [3] for all integrals.

All calculations reported have been performed on a CDC 3200 computer using programs written by one of us (BTH) in this department. The integral, SCF and one electron properties programs have all been tested against data generously supplied by J. L. Whitten and W. Fink.

Table 5. CH_4 — *Orbital energies*

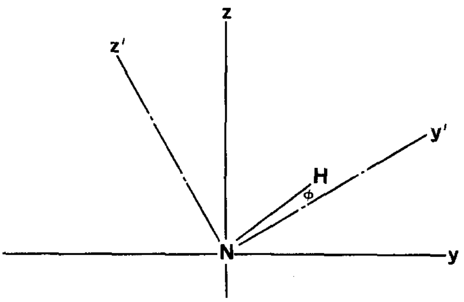
Molecular orbitals	Basis set		
	C (1222) H (3)	C (1223) H (3)	C (3435) H (5)
$1a_1$	−11.1750	−11.1693	−11.2108
$2a_1$	− 0.9607	− 0.9599	− 0.9381
$1t_2$	− 0.5101	− 0.5071	− 0.5411
E_{Tot}	−40.1074	−40.1008	−40.1672

All energies in atomic units.

Table 6. NH_3 — *One electron properties*

Property		Basis set		
		N (1222) H (3)	N (1223) H (3)	N (3435) H (5)
μ	[a]	2.54	2.67	2.31
θ_{xx}	[b]	1.116	1.184	1.143
θ_{zz}		− 2.233	− 2.367	− 2.300
$\langle x^2 \rangle$	[c]	9.256	9.138	9.210
$\langle z^2 \rangle$		7.340	7.318	7.343
$\langle r^2 \rangle$		25.85	25.59	25.76
$\left\langle \frac{1}{r} \right\rangle_N$	[c]	19.994	20.040	20.010
$\sigma^d_{av}(N)$	[d]	354.9	355.7	355.2
$\left\langle \frac{1}{r} \right\rangle_H$	[c]	5.365	5.349	5.376
$\sigma^d_{av}(H)$	[d]	95.2	94.9	95.4
$\chi^Q_{xx}(N)$	[e]	2.67	2.65	3.32
$\chi^Q_{zz}(N)$		− 5.34	− 5.29	− 6.63
$\chi^Q_{xx}(D)$	[f]	−134.8	−129.4	−128.6
$\chi^Q_{y'y'}(D)$		296.2	285.7	288.3
$\chi^Q_{z'z'}(D)$		−161.8	−156.3	−159.7
ϕ	[g]	4.2°	4.3°	2.6°

[a] In Debye units.
[b] In units of 10^{-26} esu.cm^2.
[c] In atomic units.
[d] In p.p.m.
[e] In MHz. $Q(N)$ taken as 1.47×10^{-26} esu.cm^2.
[f] In kHz.
[g] Axes.



The performance of both sets with respect to calculated total energy is very good — the deviation from the value derived with the full Whitten set being 0.03 to 0.1 % error. The implication is that for energy calculations an excellent estimate of the "double zeta" energy can be obtained with considerable computational economy by use of the mixed Gaussian basis technique illustrated here.

It should be noted that in some of the reported calculations, because of underestimations in the approximated repulsion integrals, the merged basis gives a lower energy than the "exact" calculation. As pointed out by Brown, Burden and Williams [10] the variation theorem does not apply exactly in these merged calculations and hence the method that yields numerically the lowest energy is not necessarily the best.

Likewise values of $\langle r_{\mathrm{H}}^{-1} \rangle$ are virtually identical with those derived by "double zeta" type STO calculations and seem superior to those obtained by the Brown-Burden-Williams 3G method [10] for example. Similarly excellent values are obtained for $\langle r^2 \rangle$ or quadrupole moments. However the performance with respect to computed dipole moment is inferior to minimal basis set STO calculations (or the virtually identical values obtained by the BBW-3G method [10]). This poorer performance is already inherent in the Whitten set, the present simplified procedure yielding values within 0.1 to 0.3 D of the Whitten values.

Quadrupole coupling constants appear to be much more sensitive to the approximations made although this no doubt will depend on the molecule in

Table 7. H_2O — *One electron properties*

Property		Basis set		
		O (1222) H (3)	O (1223) H (3)	O (3435) H (5)
μ	a	2.48	2.63	2.50
θ_{xx}	b	– 1.911	– 2.013	– 1.974
θ_{yy}		1.962	2.073	2.050
θ_{zz}		– 0.051	– 0.059	– –.075
$\langle x^2 \rangle$	c	5.194	5.187	5.187
$\langle y^2 \rangle$		7.377	7.265	7.296
$\langle z^2 \rangle$		6.337	6.284	6.311
$\langle r^2 \rangle$		18.91	18.74	18.79
$\left\langle \frac{1}{r} \right\rangle_{\mathrm{H}}$	d	5.759	5.740	5.755
$\sigma_{\mathrm{av}}^{d}(\mathrm{H})$	e	102.2	101.9	102.2
$\left\langle \frac{1}{r} \right\rangle_{\mathrm{O}}$	d	23.519	23.588	23.545
$\sigma_{\mathrm{av}}^{d}(\mathrm{O})$	e	417.5	418.2	417.9
$\chi_{xx}^{Q}(\mathrm{O})$	f	17.18	16.51	17.00
$\chi_{yy}^{Q}(\mathrm{O})$		– 13.89	– 13.46	– 16.25
$\chi_{zz}^{Q}(\mathrm{O})$		– 3.29	– 3.04	– 0.75
$\chi_{xx}^{Q}(\mathrm{D})$	g	–228.3	–221.8	–223.0
$\chi_{y'y'}^{Q}(\mathrm{D})$		374.2	363.2	362.9
$\chi_{z'z'}^{Q}(\mathrm{D})$		–170.2	–165.0	–176.0
ϕ	h	3.6°	3.7°	2.6°

[a] Dipole moment in Debye units.

[b] Molecular quadrupole moments relative to the centre of mass of water in units of 10^{-26} esu. cm^2 or Buckinghams.

$$\theta_{\alpha\beta} = -\frac{1}{2}\sum_i \langle \psi_i | 3r_\alpha r_\beta - \delta_{\alpha\beta} r^2 | \psi_i \rangle$$

$$+\frac{1}{2}\sum_n Z_n (3R_{n\alpha}R_{n\beta} - \delta_{\alpha\beta}R_n^2)$$

1 a.u. = 1.344911×10^{-26} esu. cm^2.

[c] Second moments in atomic units, relative to the centre of mass of water. 1 a.u. = 0.280023×10^{-16} cm^2

$$\langle \alpha\beta \rangle = \sum_i \langle \psi_i | r_\alpha r_\beta - \delta_{\alpha\beta} r^2 | \psi_i \rangle .$$

[d] In atomic units, 1 a.u. = 9.07618 esu. cm^{-1}

$$\left\langle \frac{1}{r} \right\rangle_A = \sum_i \left\langle \psi_i \left| \frac{r_{A\alpha} r_{A\beta} - \delta_{\alpha\beta} r_A^2}{r_A^3} \right| \psi_i \right\rangle .$$

[e] Average diamagnetic shielding in p.p.m.

$$\sigma^d_{av}(A) = \frac{e^2}{3mc^2} \left\langle \frac{1}{r} \right\rangle_A$$

$$= 17.75 \left\langle \frac{1}{r} \right\rangle_A \text{ p.p.m.}$$

[f] Quadrupole coupling constant in MHz at oxygen nucleus

$$\chi^Q_{\alpha\beta}(A) = \frac{eQ_A q_{\alpha\beta}}{h} = \frac{eQ_A}{h}\left[-\sum_i \left\langle \psi_i \left| \frac{3r_{A\alpha} r_{A\beta} - \delta_{\alpha\beta} r_A^2}{r_A^5} \right| \psi_i \right\rangle \right.$$

$$\left. + \sum_{n(n \neq A)} Z_n \left(\frac{3R_{n\alpha}R_{n\beta} - \delta_{\alpha\beta}R_n^2}{R_n^5} \right) \right]$$

$$= 2.3497215 \times 10^{26} Q_A q_{\alpha\beta} \text{ MHz.}$$

$q_{\alpha\beta}$ electric field gradient in atomic units. Q(O) nuclear quadrupole moment taken as -2.4×10^{-26} esu. cm^2.

[g] Quadrupole coupling constants at deuterium in kHz. Q(D) nuclear quadrupole moment taken as 0.2796×10^{-26} esu. cm^2.

[h] Molecular axes.

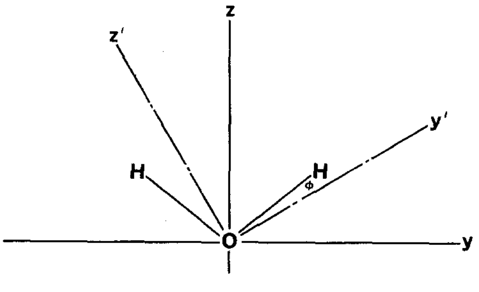


Table 8. CH_4 — *One electron properties*

Properties		Basis sets		
		C (1222) H (3)	C (1223) H (3)	C (3435) H (5)
$\langle z^2 \rangle$	[a]	11.88	11.87	11.93
$\langle r^2 \rangle$		35.65	35.61	35.79
$\left\langle \frac{1}{r} \right\rangle_C$	[a]	16.697	16.703	16.681
$\sigma^d_{av}(C)$	[b]	296.4	296.5	296.1
$\left\langle \frac{1}{r} \right\rangle_H$	[a]	4.883	4.881	4.908
$\sigma^d_{av}(H)$	[b]	86.7	86.6	87.1
$\chi^Q_{zz}(D)$	[c]	227.5	226.6	231.4

[a] In atomic units.
[b] In p.p.m.
[c] In kHz.

question. For the three molecules tested, the quadrupole coupling constants for deuterium are relatively insensitive to the approximations made. This result is expected since the field gradient at deuterium is primarily due to the influence of neighbouring atoms and, therefore, will be less sensitive to changes in the basis set.

At heavy atoms one expects the field gradient to be very dependent on the representation of the charge density about the nucleus and therefore to be much more sensitive to changes in the basis set used. The results indiacte that the approximations employed in this work have a large effect on the coupling constants for oxygen and further investigation is in progress to ascertain whether this poorer representation of the heavy atom charge density is generally observed or unique to the water molecule.

We have only reported calculations in which the (1 2 2 2) and (1 2 2 3) basis sets were used for the multicentre repulsion integrals although calculations using the sets (2 2 2 2), (2 2 2 3), (1 2 1 2) and (1 2 1 3) have been completed. Our investigations indicate that changes in the size of the *S* groups affect the calculated properties much less than when the size of the *P* group is altered. In view of the substantial increase in computer time when the (1 2 2 3) set is employed, we propose to use the (1 2 2 2) set in future investigational work.

For the exploratory calculations described here, employing small molecules where the 3- and 4-centre integrals do not overwhelmingly dominate the computing time, we find that the percentage reduction in time by using the merging procedure is almost equal to the percentage of non-zero 3- and 4-centre integrals. Thus in *ab initio* calculations on large polyatomic molecules one could expect up to a 50 percent time reduction if the method described here were used.

Provided that the performance found here is maintained in calculations on larger molecules, this time reduction, coupled with the excellent correspondence of results with those from the full calculations, would make it difficult to justify the much greater computational costs of SCFMO calculations using large Gaussian lobe sets without the use of smaller basis sets for 3- and 4-centre integrals.

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