Theoret. chim. Acta (Berl.) 22, 378 – 385 (1971)

Small Gaussian Basis Sets for Second-Row Atoms

T. A. CLAXTON and N. A. SMITH

Department of Chemistry, The University, Leicester, LE1 7RH, England

Received March 29, 1971

6*s*-type and 4*p*-type gaussian basis sets are obtained for the second row atoms by fitting, using a least squares criterion, to 12*s*-type and 9*p*-type gaussian basis sets which are close to the self-consistent field atomic orbital wave functions. The small gaussian expansions are considered to be more suited for molecular calculations using double basis sets. The differences between these sets and the 10*s*-type, 6*p*-type and 9*s*-type, 5*p*-type are analysed. For molecular calculations using single gaussian basis sets the 10*s*-type and 6*p*-type would seem to be the best compromise.

Ein Basissatz von Gaußfunktionen vom 6*s*- bzw. 4*p*-Typ für Atome der zweiten Reihe wird erhalten, indem die Funktionen mit Hilfe des Kriteriums der kleinsten quadratischen Abweichung einem Satz von Gaußfunktionen vom 12*s*- bzw. 9*p*-Typ angepaßt werden; dabei ist der letztgenannte Satz der selbstkonsistenten Wellenfunktion aus Atomorbitalen stark angenähert. Die kürzeren Entwicklungen nach Gaußfunktionen werden für geeigneter bei Berechnungen mit „zweifachen" Basissätzen gehalten. Die Unterschiede zwischen diesen Sätzen und solchen vom 10*s*- bzw. 6*p*-Typ sowie vom 9*s*- und 5*p*-Typ werden untersucht. Für Molekülrechnungen mit „einfachen" Basissätzen von Gaußfunktionen scheint der Satz vom 10*s*- bzw. 6*p*-Typ den besten Kompromiß darzustellen.

On obtient des bases gaussiennes de type 6*s* et 4*p* pour les atomes de la seconde ligne par ajustement selon un critère de moindre carré à des bases gaussiennes de type 12*s* et 9*p* proches des orbitales atomiques SCF. Les petits développements en gaussiennes sont plus adaptés à des calculs moléculaires en bases doubles. Analyse des différences entre cas bases et les bases de types 10*s* et 6*p*, 9*s* et 5*p*. Pour des calculs moléculaires à base simple, 10*s* et 6*p* semble le meilleur compromis.

Introduction

Ever since Boys [1] pointed out the advantages of Boys (gaussian) type orbitals (GTO) over Slater (exponential) type (STO) orbitals, particularly in the evaluation of multicentre two electron orbitals, a considerable amount of effort has been directed at finding suitable gaussian expansions for Slater type and atomic SCF (self-consistent field) orbitals. Clementi and Davis [2] have outlined the procedures for using gaussians. Huzinaga [3] developed methods to obtain the gaussian exponents and expansion coefficients for the GTO's, using the criteria of minimum energy or least squares fit with an STO. The vast majority of computing time is spent evaluating the large number of two-electron integrals; in fact proportional to N^4 where N is the number of gaussian functions in the calculation. Cook and Palmieri [4] noted that small expansions of gaussian functions were satisfactory for the multi-centre two-electron integrals, but much larger expansions were necessary to reproduce the values of the one-electron integrals. For this reason Cook and Palmieri [4] suggested using STO's for the one-electron and one centre integrals and small gaussian expansion representations of the STO's for the multicentre electron integrals, and so formulated the "mixed" basis method. Since this method is STO oriented it is convenient to distinguish that method which is SCF orbital oriented as the "double" basis method. The philosophy of the "double" basis method is identical to the mixed basis method; large gaussian expansion representations of SCF orbitals are used for all one-electron and one centre integrals and small gaussian expansions for the multi-centre two-electron integrals. It is to be distinguished from the "combined basis" method of Silver [14] which augments STO basis sets with GTO basis sets.

For the first, second and third row atoms a number of gaussian expansion representations of SCF atomic orbitals in the ground state exist, using the criterion of either energy minimisation [3, 5–10], or a least squares [3, 11, 12] fit. In the "double" basis method the "best" gaussian representation, using the criterion of energy minimisation, is chosen to calculate all the one-centre and one-electron integrals. This is invariably the largest available expansion in each case. However, for the multi-centre two-electron integrals these are integrals of solely molecular origin and the criterion of energy minimisation, to optimise the gaussian parameters in the orbital representations of the atoms, does not seem appropriate for the small expansions. This is because the energy is very dependent on the wave function close to the nucleus, whereas most of the multi-centre two-electron integrals depend on the electron density distribution remote from the nuclei. The view taken here is that it is a more satisfactory procedure to fit the small expansion to the large expansion by a least squares criterion.

Method

The 12s-type, 9p-type contracted gaussian expansion representations for the atomic SCF orbitals of the second row atoms due to Veillard [6] were used as the standard functions to which other gaussian expansion were to be compared or fitted by a least squares procedure. Any gaussian expansion of the radial part of an orbital can be expressed as ($n=0$ for s, $n=1$ for p)

$$\chi_i = \sum_j c_{ij} r^n \exp(-\alpha_j r^2) \tag{1}$$

where $\boldsymbol{r}$ is the distance from the nucleus on which the orbital is centred. For all orbitals with the same spherical harmonic on an atom the exponents, α_j, are the same for all χ_i. This restriction is important since it considerably reduces the time required to evaluate the two-electron integrals, and limits the usefulness of the orbitals of Stewart and Hehre [12]. Since two gaussian functions per orbital were considered to be the minimum necessary to obtain a reasonable least squares fit, six terms in Eq. (1) were used to represent the s orbitals and four terms for the p orbitals. In the case of sodium and magnesium where there is only one p orbital three gaussian functions were required to obtain a comparable least squares fit.

The problem is to minimise the error function

$$\varepsilon = \sum_i \int (\psi_i - \chi_i)^2 \, d\tau \tag{2}$$

where the summation i extends over all functions of a particular spherical harmonic, ψ represents one of the standard functions due to Veillard, and $\int \chi_i \chi_j d\tau = \delta_{ij}$.

Although methods have been given to minimise this type of function (Eq. (2)), it proved convenient, in view of the multiple minima commonly encountered in such problems, to use a regression method programmed in ALGOL [13]. Crudely the function is evaluated many times over varying limits of the variables c and α, such that ε is always reduced. In spite of the considerable effort expended to obtain the true minima, no such guarantee can be given in common with the other methods.

Table 1. *Orbital exponents for the atoms* Na–Cl

	Na	Mg	Al	Si	P	S	Cl
1*s*	111.227	134.844	161.147	189.876	220.942	254.622	291.089
	19.3927	23.5833	28.2602	33.3739	38.9184	44.9307	51.4563
	2.03032	2.65013	3.36996	4.17415	5.13708	6.06132	7.21092
	.673459	.939751	1.25741	1.61353	2.02664	2.44758	2.94131
	.0568152	.106827	.174090	.250321	.331263	.419642	.517819
	.0243412	.0401781	.0654338	.0937598	.124194	.156061	.192321
2*p*	10.4051	13.8296	9.18018	11.6797	14.3844	17.2573	20.3878
	2.26735	3.07812	1.82337	2.39028	3.01217	3.67964	4.41311
	.574517	.814328	.193724	.291788	.400179	.511454	.637749
			.0536952	.0825787	.114423	.140106	.172008

Table 2. *Expansion coefficients for the atoms* Na–Cl

	Na	Mg	Al	Si	P	S	Cl
1*s*	0.378210	0.372851	0.367474	0.362817	0.358876	0.355074	0.351338
	0.697320	0.697434	0.697575	0.697624	0.697342	0.697401	0.697074
	0.084284	0.093982	0.103659	0.111729	0.115935	0.124378	0.129717
	−0.032257	−0.037668	−0.043273	−0.047613	−0.046093	−0.053328	−0.054849
	0.008934	0.010091	0.012263	0.013730	0.007312	0.015265	0.015730
	−0.005246	−0.005141	−0.005956	0.006441	0.000001	−0.006884	−0.007110
2*s*	−0.104184	−0.105331	−0.106082	−0.106727	−0.107222	−0.107728	−0.107799
	−0.276630	−0.289290	−0.299778	−0.308422	−0.316083	−0.321839	−0.327381
	0.543841	0.469994	0.452238	0.415975	0.375296	0.357385	0.326797
	0.556180	0.596233	0.633101	0.662821	0.697771	0.711525	0.737404
	0.022404	0.028578	0.037871	0.045339	0.052796	0.056716	0.062328
	−0.010794	−0.011549	−0.013521	−0.014694	−0.016151	−0.016245	−0.017146
3*s*	0.016503	0.020774	0.024925	0.027731	0.029785	0.031533	0.032815
	0.041178	0.056729	0.071391	0.082090	0.090767	0.098266	0.104607
	−0.087001	−0.112107	−0.127774	−0.134300	−0.132705	−0.138088	−0.134064
	−0.219744	−0.270223	−0.328948	−0.371407	−0.407006	−0.431636	−0.457898
	0.611708	0.599934	0.610159	0.606418	0.610698	0.629231	0.633463
	0.467648	0.510779	0.524553	0.545350	0.551965	0.544829	0.547990
2*p*	0.249157	0.237312	0.468740	0.451130	0.439155	0.431414	0.424827
	0.575825	0.576580	0.670879	0.677276	0.681179	0.683585	0.685526
	0.403887	0.403673	0.072095	0.080276	0.085020	0.086286	0.087835
			−0.022476	−0.023452	−0.023960	−0.022268	−0.021280
3*p*			−0.093948	−0.108112	−0.117761	−0.125725	−0.131960
			−0.110451	−0.134132	−0.150631	−0.158374	−0.166499
			0.523496	0.541227	0.556305	0.573525	0.584599
			0.595584	0.578746	0.565310	0.556031	0.548826

Results

The orbital exponents, α, are given in Table 1. In Table 2 the corresponding expansion coefficients are listed. Orbital energies have not been calculated, or the total energy, since these orbitals are not intent to be used in "single" basis set calculations. The error function

$$\varepsilon_i = \int (\phi_i - \xi_i)^2 \, d\tau \tag{3}$$

was evaluated for various functions (Table 3) where ϕ_i and ξ_i are any pair of the gaussian expansion representations of SCF atomic orbitals as calculated by Veillard [6] (12*s*, 9*p*), Roos and Siegbahn [7] (10*s*, 6*p*), Huzinaga, McWilliams and Domsky [10] (9*s*, 5*p*) and this work (6*s*, 4*p*). Some clarification of the nature of the fit is given in Figs. 1 and 2.

Discussion

The 3*s* orbitals from the 6*s*, 4*p* gaussian set deviate (see Fig. 1) from the 12*s*, 9*p* set in a manner which is to be expected from a least squares fit. The deviation for the 3*p* orbitals is not characteristic of a least squares fit, showing a small positive fluctuating deviation near the nucleus (the 2*p* orbitals show negative deviations in this region). In all cases the fit of the 6*s*, 4*p* set to the 12*s*, 9*p* set is very

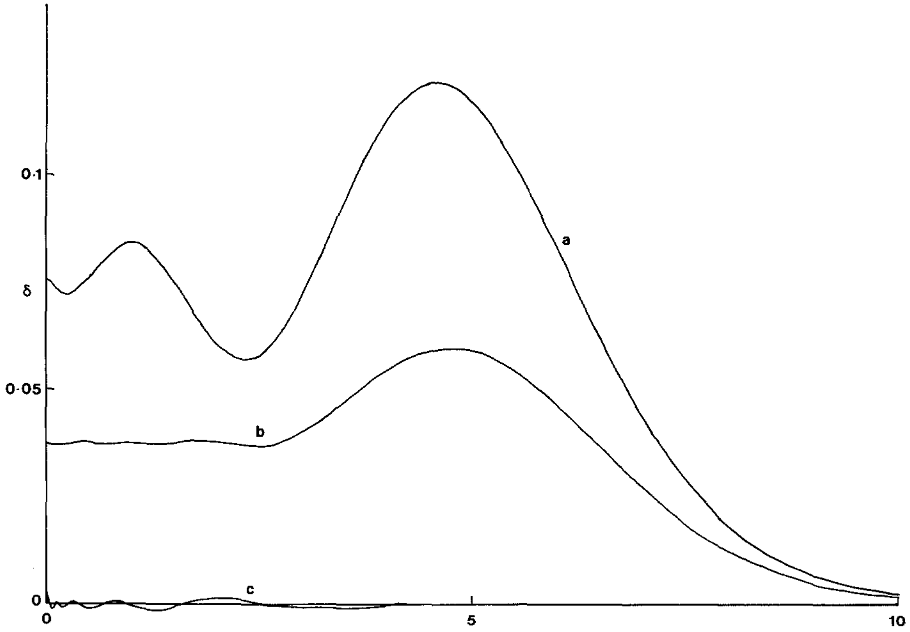

Fig. 1. Variation of the difference, $\delta(=\psi_{3s} - \chi_{3s})$ as a function of the distance, *r*, from the nucleus for the aluminium atom. a) χ corresponds to Huzinaga *et al.* [10] expansion; b) χ corresponds to Roos and Siegbahn [7] expansion; c) χ corresponds to gaussian expansion in this work

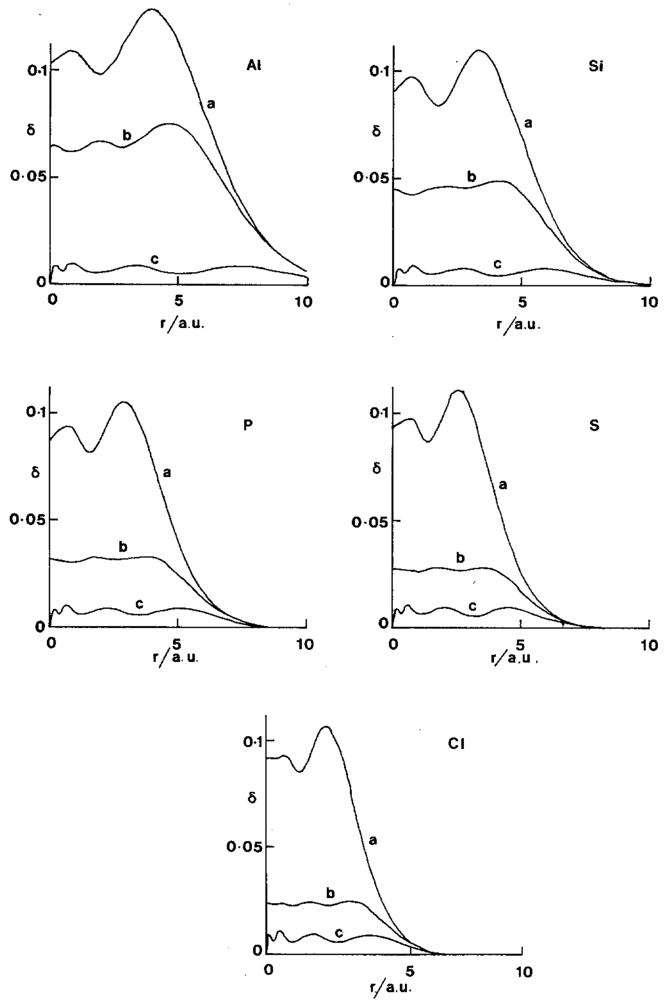

Fig. 2. Variation of the difference, $\delta(=\psi_{3p}-\chi_{3p})$ as a function of the distance, r, from the nucleus for the atoms indicated. a) χ corresponds to Huzinaga *et al.* [10] expansion; b) χ corresponds to Roos and Siegbahn [7] expansion; c) χ corresponds to gaussian expansion in this work

good, the maximum deviation being about 0.01. Although the 9*s*, 5*p* set and the 10*s*, 6*p* set have been calculated by using a minimum energy criterion, it would seem, assuming that the 12*s*, 9*p* set is the best available, that for molecular calculations the 10*s*, 6*p* set might be a good compromise. The reasons are twofold;

(i) the maximum deviation of the 10*s*, 6*p* set is less than half that for the 9*s*, 5*p* set in all cases, except for aluminium (ii) since the number of integrals to be evaluated is proportional to N^4 where N is the number of *s* or *p*-type gaussians, the saving in time by using a 10*s*, 6*p* set is considerable compared with the 12*s*, 9*p* set.

The similarity in the plots for the deviations for the 3*p* orbitals of each atom (Fig. 2) suggest that the orbitals discussed here are consistent amongst themselves.

Table 3. *Values of the error function defined in Eq.* (3) *for all the orbitals of the second row elements*

1*s* orbitals

	Veillard	Roos	Huzinaga	This work	Veillard	Roos	Huzinaga	This work
Veillard [6]	Mg Na	0.0000366	0.0000453	0.0024293	Si Al	0.0000369	0.0000423	0.0021710
Roos [7]	0.0000115		0.0000047	0.0023263	0.0000557		0.0000015	0.0020655
Huzinaga [10]	0.0000534	0.0000034		0.0023064	0.0000604	0.0000019		0.0020455
This work	0.0022994	0.0022046	0.0021675		0.002094	0.0019835	0.0019883	
Veillard	S P	0.0000459	0.0000490	0.0020073	Cl	0.0002253	0.0002315	0.0019007
Roos	0.0000412		0.0000033	0.0019110			0.0000032	0.0018164
Huzinaga	0.0000456	0.0000041		0.0019132				0.0018094
This work	0.0019418	0.0018702	0.0018679					

2*s* orbitals

	Veillard	Roos	Huzinaga	This work	Veillard	Roos	Huzinaga	This work
Veillard	Mg Na	0.0001043	0.0002211	0.0001985	Si Al	0.0000515	0.0001755	0.0002354
Roos	0.0000322		0.0001313	0.0001881	0.0000588		0.0001499	0.0001976
Huzinaga	0.0001901	0.0000997		0.0002774	0.0001810	0.0006951		0.0003074
This work	0.0002263	0.0001974	0.0002807		0.0002802	0.0002261	0.0003342	
Veillard	S P	0.0000448	0.0001748	0.0002892	Cl	0.0001018	0.0001532	0.0003138
Roos	0.0000468		0.0001409	0.0002318			0.0002418	0.0002782
Huzinaga	0.0001491	0.0001339		0.0003634				0.0003853
This work	0.0002864	0.0002087	0.0003655					

3*s* orbitals

	Veillard	Roos	Huzinaga	This work	Veillard	Roos	Huzinaga	This work
Veillard	Mg Na	0.0006633	0.0035591	0.0000258	Si Al	0.0013400	0.0061654	0.0000358
Roos	0.0000214		0.0019415	0.0006109	0.0035036		0.0020133	0.0013100
Huzinaga	0.0066465	0.0065223		0.0035302	0.0062949	0.0006951		0.0061549
This work	0.0000304	0.0000248	0.0066274		0.0030347	0.0034899	0.0063047	
Veillard	S P	0.0000507	0.0062906	0.0000456	Cl	0.0005693	0.0063677	0.0000591
Roos	0.0001167		0.0061127	0.0000385			0.0045287	0.0005110
Huzinaga	0.0063753	0.0058982		0.000306				0.0063990
This work	0.0000500	0.0000900	0.0063963					

Table 3 (continued)

2p orbitals

	Veillard	Roos	Huzinaga	This work	Veillard	Roos	Huzinaga	This work
Veillard	Mg Na	0.0010358	0.0001982	0.00125523	Si Al	0.0001273	0.0007272	0.0063254
Roos	0.0007999		0.0005031	0.0011522	0.0001850		0.0007584	0.0060464
Huzinaga	0.0001171	0.0004877		0.0009492	0.0004174	0.0005498		0.0060598
This work	0.0010682	0.0008792	0.0008481		0.0053708	0.00476218	0.0055275	
Veillard	S P	0.0002171	0.0003341	0.0047765	Cl	0.0001949	0.0001709	0.0041166
Roos	0.0001929		0.0004376	0.0041197			0.0003598	0.0036284
Huzinaga	0.0002575	0.0003426		0.0050204				0.0045263
This work	0.0041206	0.0038468	0.0047051					

3p orbitals

	Veillard	Roos	Huzinaga	This work	Veillard	Roos	Huzinaga	This work
Veillard	Mg Na				Si Al	0.0197262	0.0527943	0.0011314
Roos					0.0091803		0.0177840	0.0215377
Huzinaga					0.0416993	0.0217828		0.0545237
This work					0.0010959	0.0095695	0.0435523	
Veillard	S P	0.0042857	0.0378756	0.001802	Cl	0.0027914	0.0372887	0.0014866
Roos	0.0034052		0.0271050	0.0038846			0.0309090	0.0020286
Huzinaga	0.0409963	0.0324924		0.00398127				0.0401473
This work	0.0014033	0.0027438	0.0433244					

An Application

We have done a series of *ab initio* UHF double basis calculations on AlH_3^- in order to verify the assignment of this radical to a species observed by electron spin resonance spectroscopy [16]. The double basis method is attractive for these calculations since the evaluation of spin density at a nucleus requires in the first place orbitals which describe the electron density at the nucleus accurately. Therefore the 12*s*-type and 9*p*-type gaussian representations of Veillard [6] are used as the basis orbitals for aluminium to evaluate all the one-electron integrals. Previous work [17] has shown that in order to obtain consistently good agreement with experiment it is at least necessary to i) remove the contaminating quartet spin state from the energy minimised UHF wave function by annihilation [18], ii) optimise the hydrogen atomic orbital exponent, iii) optimise all bond lengths involving hydrogen atoms. Optimisation is a time consuming operation but using the orbitals described in this paper for all the multicentre two-electron integrals the time required is less than one sixteenth that needed for the single basis method using Veillard's [6] orbitals. Using the double basis method it was calculated that $R(\mathrm{Al–H}) = 3.2$ a.u., the optimised hydrogen orbital exponent $\alpha = 1.0$, the molecule is pyramidal, each Al–H bond making an angle of 21° with the plane perpendicular to the three fold axis, the isotropic hyperfine coupling constants after spin annihilation are $a(^{27}\mathrm{Al}) = 213.8\ G$, $a(^{1}\mathrm{H}) = 3.5\ G$, and the total energy after spin annihilation is $E = -243.57247$ a.u. The available experimental data is $a(^{27}\mathrm{Al}) = 223\ G$, $a(^{1}\mathrm{H}) < 20\ G$ with a derived out-of-plane angle of $\sim 19°$. The agreement is excellent and provides theoretical evidence for the existence of AlH_3^-. The smallness of the calculated proton coupling constant is reassuring since the small magnitude observed experimentally was thought surprising and was not used in support of the identification.

Acknowledgements. The award of an S.R.C. studentship to N.A.S. and computing assistance from Mrs. C. A. Crane are gratefully acknowledged.

References

1. Boys, S. F.: Proc. Roy. Soc. (Lond.) A **200**, 542 (1950).
2. Clementi, E., Davies, D. R.: J. comput. Physics **1**, 223 (1966).
3. Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).
4. Cook, D. B., Palmieri, P.: Molecular Physics **17**, 275 (1969).
5. Whitman, D. R., Hornback, C. J.: J. chem. Physics **51**, 398 (1969).
6. Veillard, A.: Theoret. chim. Acta (Berl.) **12**, 405 (1968).
7. Roos, B., Siegbahn, P.: Theoret. chim. Acta (Berl.) **17**, 209 (1970).
8. Wachters, A. J. H.: J. chem. Physics **52**, 1033 (1970).
9. Basch, H., Hornback, C. J., Moskowitz, J. W.: J. chem. Physics **51**, 1311 (1969).
10. Huzinaga, S., McWilliams, D., Domsky, B.: J. chem. Physics (in press).
11. Stewart, R. F.: J. chem. Physics **50**, 2485 (1969).
12. — Hehre, W. J.: J. chem. Physics **52**, 5243 (1970).
13. Weinmann, A.: unpublished.
14. Silver, D. M.: Chem. Physics Letters **7**, 511 (1970).
15. Allen, L. C.: J. chem. Physics **31**, 736 (1959).
16. Catton, R. C., Symons, M. C. R.: J. chem. Soc. A **1969**, 2001.
17. Claxton, T. A.: Trans. Faraday Soc. **66**, 1537 (1970).
18. Amos, A. T., Hall, G. G.: Proc. Roy. Soc. A **263**, 483 (1961).

Dr. T. A. Claxton
Department of Chemistry
The University
Leicester, LE1 7RH, England