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Comparison of Cartesian and Lobe Function Gaussian Basis Sets

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The lobe function and cartesian (spherical harmonic) gaussian are compared with reference to calculations for second-row atoms. Single and grouped gaussian basis sets which have been reported for cartesian functions are taken over directly to construct corresponding lobe function bases with identical sets of exponents and with lobe separations chosen by a scaling procedure. Total and orbital energies and SCF coefficients resulting from calculations on the second-row atoms using the two types of functions for both primitive and grouped gaussian basis sets are seen to be in excellent agreement, thereby emphasizing the essential equivalence of lobe functions and cartesian gaussians, at the very least with respect to calculation of energy surfaces.

Die Lobe-Funktionen und kartesischen (Kugelfunktions-) Gaußfunktionen werden in Berechnungen von Atomen der zweiten Reihe des periodischen Systems verglichen. Schon bekannte einfache und gruppierte Gaußfunktionsbasissätze für kartesische Funktionen werden direkt übernommen, um entsprechende Lobe-Funktionsbasen mit identischen Exponenten zu konstruieren, wobei die zugehörigen Lobe-Abstände nach einer Koordinatenstreckungs- (scaling) Methode berechnet werden. Gesamt- und Orbitalenergien sowie SCF-Koeffizienten für die Atome der zweiten Reihe stimmen bei Benutzung der beiden verschiedenen Funktionstypen, sowohl bei einfacher als auch bei gruppierter Gaußfunktionsbasis, außerordentlich gut überein, wodurch die wesentliche Gleichwertigkeit von Lobe-Funktionen und kartesischen Gaußfunktionen betont wird, zum allermindesten hinsichtlich der Berechnung von Energieflächen.

La fonction de lobe et la gaussienne cartésienne (harmonique sphérique) sont comparées sur des calculs d'atomes de la seconde ligne. Des bases de gaussiennes simples et groupées utilisées pour les fonctions cartésiennes sont directement employées pour construire les bases correspondantes de fonctions à lobes avec des ensembles d'exposants identiques et des séparations de lobes choisis par calibrage. L'emploi de ces deux types de fonctions donne des résultats concordants pour l'énergie totale, les énergies orbitales et les coefficients SCF, mettant l'accent sur l'équivalence essentielle des fonctions à lobe et des gaussiennes cartésiennes, tout au moins pour le calcul des surfaces d'énergie.

1. Introduction

The suggestion that gaussian functions $\exp(-\alpha r^2)$ be employed to describe the radial behaviour of electronic wavefunctions [1] has led to a marked increase in activity in the area of *a priori* calculations for polyatomic molecules. The success of this approach rests in great part upon the tractability of the general multicenter electron repulsion integrals resulting from the use of such functions. While simple exponential functions $\exp(-\xi r)$ have also been used successfully for the treatment of small polyatomics, for larger molecules *a priori* calculations to date have been restricted entirely to those employing gaussians. Recently systems the size of azulene and naphthalene [2] have been studied *ab initio* using a gaussian basis set which is capable of obtaining a good approximation to the Hartree-Fock solutions of the constituent atoms; smaller basis set calculations of this type have also been reported for biologically important systems, such as adenine [3], and also for naphthalene [4].

Attempts to achieve the proper angular dependence for these gaussian functions have proceeded along two different lines. The first involves multiplication of the radial term by the appropriate spherical harmonic $Y_{lm}(\theta, \phi)$, in direct analogy to the construction of the Slater-type or simple exponential AO; this function is commonly referred to as the cartesian gaussian:

$$g_{lm}^{C} = N_l^C r^l \exp(-\alpha r^2)\, Y_{lm}(\theta, \phi) \quad \text{(normalized)}. \tag{1}$$

Preuss [5], on the other hand, has proposed that the desired angular characteristics can also be obtained by taking linear combinations of simple gaussians rather than by multiplying them with spherical harmonics; these sums of gaussians are referred to as lobe functions and can be discussed most conveniently with reference to real p-type combinations:

$$g_p^L(\hat{y}) = N_p^L \{\exp[-\alpha(\boldsymbol{r} - R_0\hat{y})^2] - \exp[-\alpha(\boldsymbol{r} + R_0\hat{y})]^2\} \tag{2}$$

where $\hat{y}$ is a unit vector, and R_0 is a constant defining the distance from the origin (usually, but not necessarily a nuclear coordinate) of the centers for the two simple gaussians. Higher spherical harmonic terms are then associated with appropriate multiples of the p-type lobe functions while the definition of an s-type gaussian in this formulation is the same as that used in connection with the cartesian functions.

An apparent disadvantage of the gaussian lobe function is its dependence upon the choice of the parameter R_0, but some insight into this question can be gained by comparison with cartesian gaussians. Variation of the exponent in Eq. (1) from α to $\alpha' = \eta^2\alpha$ can be conveniently looked upon as a two-step process which involves scaling the distance coordinate by η and then renormalizing. If the same procedure is utilized for exponent variation for the p-type lobe function of Eq. (2) it follows that not only does $\alpha' = \eta^2\alpha$ but also $R_0' = R_0\eta^{-1}$ and thus that $R_0\alpha^{\frac{1}{2}} = R_0'\alpha'^{\frac{1}{2}}$ is a constant, hereafter referred to as c, independent of the value of the exponent. By substitution of $c\alpha^{-\frac{1}{2}}$ for R_0 in Eq. (2) followed by expansion of this function in a Taylor series about the origin [6] one obtains an expression for g_p^L whose leading term differs by only a constant factor from the corresponding *real* cartesian function.

The other terms in this Taylor series expansion depend on even powers of the constant c and therefore theoretically can be made as small as desired with respect to the leading term simply by choosing c to be arbitrarily small. In practice, however, a *relatively large* value of this parameter must be chosen to insure the required precision in the calculation of the various electron repulsion and one-electron integrals and thus it is necessary to examine the aforementioned series in more detail. If c has a typical value of 0.03, for example, for $\alpha = 100$ the second term evaluated at a distance of 1.0 a.u. from the origin is 6% of the first term of the series; indeed at larger distances the angular part of the Taylor series must diverge from the desired spherical harmonic from, regardless of the choice of the constant c (except for the trivial case of vanishing c). Although the radial part $\exp(-\alpha r^2)$ acts as a strongly damping factor at such distances, this property would seem to raise serious questions about the utility of the gaussian lobe functions; in particular it would appear that its transformation properties might be significantly different from those of its cartesian analog because of the presence of higher order spherical harmonic terms in the aforementioned expansion. In order to examine these questions the present paper thus attempts a comparison of the two types of gaussian functions with reference to their use in atomic calculations.

2. Comparison of Primitive Gaussian Basis Sets

A first attempt at comparing cartesian and lobe function gaussians involves the single or primitive gaussian basis sets for second-row atoms reported by Veillard [7]. For each of these systems the identical set of exponents employed in the cartesian basis is chosen for the corresponding lobe function set; the lobe separation R_0 for each of the p functions is related to its exponent by the expression $R_0 = c\alpha^{-\frac{1}{2}}$, with c fixed at a value of 0.03, so that differences in exponent in both cases can be looked upon as resulting from a scaling procedure (see Introduction). A comparison of the resulting total energies of these atoms is given in Table 1 while corresponding orbital energies and SCF expansion coefficients are given in Table 2.

For each atom the total energies are seen to agree to at least seven significant figures, with the largest discrepancy occuring for phosphorus and of magnitude 6.0×10^{-5} hartree. The cartesian basis sets consistently produce the lower energy, with only one slight exception noted in sodium. Such agreement would seem to be remarkably good in view of the different functions employed; it would not be at all implausible to argue that a significant portion of the

Table 1. *Comparison of total energies for the atoms* Na *through* Ar *obtained from cartesian and lobe function single gaussian* (12, 9) *basis sets using identical exponents, given by Veillard. (Throughout this paper all energy values are given in hartrees)*

	Cartesian basis[a]	Lobe function basis
Na	−161.85259	−161.85260
Mg	−199.60777	−199.60776
Al	−241.87118	−241.87117
Si	−288.84857	−288.84855
P	−340.71213	−340.71207
S	−397.49776	−397.49773
Cl	−459.47405	−459.47402
Ar	−526.80828	−526.80827

[a] Ref. [7].

Table 2. *Orbital energies and* SCF AO *expansion coefficients for* Na *through* Ar *obtained from Veillard's cartesian and the corresponding lobe function single gaussian basis sets*

	Na(^2S)		Mg(^1S)		Al(^2P)		Si(^3P)	
	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe
1*s*	−40.4758	−40.4758	−49.0290	−49.0288	−58.4999	−58.5003	−68.8110	−68.8116
	0.00038	0.00039	0.00038	0.00038	0.00035	0.00035	0.00031	0.00031
	0.00305	0.00305	0.00293	0.00294	0.00275	0.00275	0.00249	0.00249
	0.01599	0.01599	0.01496	0.01497	0.01418	0.01419	0.01303	0.01304
	0.06427	0.06426	0.05863	0.05863	0.05585	0.05585	0.05227	0.05227
	0.19481	0.19482	0.17661	0.17662	0.16789	0.16789	0.16151	0.16151
	0.40099	0.40099	0.37113	0.37112	0.35419	0.35419	0.34767	0.34768
	0.39267	0.39266	0.40079	0.40083	0.40028	0.40028	0.40445	0.40445
	0.08282	0.08288	0.12384	0.12379	0.15029	0.15029	0.16243	0.16243
	−0.00265	−0.00270	0.00375	0.00379	0.00759	0.00759	0.00914	0.00915
	0.00177	0.00179	0.00052	0.00051	−0.00032	−0.00033	−0.00067	−0.00067
	−0.00031	−0.00032	−0.00003	−0.00005	0.00017	0.00018	0.00025	0.00026
	0.00017	0.00018	0.00001	0.00004	−0.00008	−0.00007	−0.00011	−0.00012
2*s*	−2.79516	−2.79517	−3.76584	−3.76568	−4.90963	−4.90987	−6.15531	−6.15572
	−0.00009	−0.00009	−0.00009	−0.00010	−0.00009	−0.00010	−0.00008	−0.00008
	−0.00074	−0.00074	−0.00073	−0.00074	−0.00071	−0.00071	−0.00066	−0.00066
	−0.00396	−0.00396	−0.00384	−0.00385	−0.00374	−0.00375	−0.00352	−0.00352
	−0.01613	−0.01613	−0.01514	−0.01515	−0.01482	−0.01483	−0.01419	−0.01419
	−0.05310	−0.05311	−0.04979	−0.04979	−0.04859	−0.04859	−0.04764	−0.04765
	−0.12776	−0.12775	−0.11832	−0.11833	−0.11480	−0.11479	−0.11479	−0.11478
	−0.19952	−0.19952	−0.20111	−0.20111	−0.19991	−0.19991	−0.20269	−0.20269
	0.03427	0.03428	−0.02310	−0.02311	−0.05228	−0.05230	−0.06623	−0.06620
	0.59803	0.59803	0.57420	0.57425	0.55218	0.55212	0.54349	0.54335
	0.48579	0.48579	0.53517	0.53513	0.56269	0.56277	0.57276	0.57292
	0.01663	0.01664	0.02118	0.02123	0.02743	0.02740	0.03119	0.03112
	−0.00762	−0.00763	−0.00801	−0.00804	−0.00885	−0.00884	−0.00869	−0.00866

3*s*	−0.18174	−0.18174	−0.25270	−0.25265	−0.39313	−0.39318	−0.53936	−0.53943
	0.00001	0.00001	0.00001	0.00002	0.00002	0.00002	0.00002	0.00002
	0.00011	0.00011	0.00014	0.00014	0.00016	0.00016	0.00016	0.00017
	0.00060	0.00061	0.00074	0.00074	0.00086	0.00087	0.00090	0.00090
	0.00241	0.00242	0.00291	0.00291	0.00342	0.00342	0.00365	0.00365
	0.00822	0.00823	0.00971	0.00972	0.01132	0.01131	0.01228	0.01227
	0.01915	0.01915	0.02298	0.02297	0.02696	0.02694	0.03007	0.03006
	0.03311	0.03311	0.04123	0.04127	0.04861	0.04858	0.05434	0.05430
	−0.01052	−0.01053	0.00306	0.00304	0.01273	0.01274	0.01926	0.01927
	−0.09898	−0.09898	−0.13501	−0.13505	−0.16340	−0.16335	−0.18536	−0.18527
	−0.20686	−0.20687	−0.25490	−0.25493	−0.30809	−0.30787	−0.34190	−0.34149
	0.59948	0.59950	0.59531	0.59491	0.60750	0.60646	0.60651	0.60482
	0.48401	0.48400	0.52058	0.52082	0.53539	0.53633	0.55734	0.55881
2*p*	−1.51611	−1.51611	−2.28022	−2.28006	−3.21727	−3.21755	−4.25486	−4.25534
	0.00513	0.00514	0.00475	0.00476	0.00407	0.00408	0.00354	0.00354
	0.03791	0.03793	0.03462	0.03464	0.03048	0.03050	0.02754	0.02756
	0.15341	0.15348	0.14372	0.14379	0.12689	0.12696	0.11649	0.11655
	0.35313	0.35319	0.34665	0.34673	0.31355	0.31364	0.29330	0.29338
	0.45550	0.45549	0.46489	0.46489	0.43981	0.43982	0.43275	0.43277
	0.24372	0.24360	0.24109	0.25096	0.28558	0.28546	0.30572	0.30561
					0.03353	0.03348	0.04573	0.04566
					−0.00564	−0.00563	−0.00389	−0.00388
					0.00192	0.00192	0.00151	0.00151
3*p*					−0.20972	−0.20981	−0.29670	−0.29686
					−0.00073	−0.00074	−0.00075	−0.00076
					−0.00549	−0.00550	−0.00593	−0.00594
					−0.02361	−0.02363	−0.02566	−0.02568
					−0.05845	−0.05848	−0.06608	−0.06612
					−0.08897	−0.08900	−0.10235	−0.10238
					−0.05068	−0.05064	−0.07229	−0.07225
					0.22619	0.22642	0.20252	0.20275
					0.54403	0.54423	0.56412	0.56435
					0.37439	0.37396	0.38465	0.38423

Table 2 (continued)

	P(^4S)		S(^3P)		Cl(^2P)		Ar(^1S)	
	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe
1s	−79.9684	−79.9692	−92.0028	−92.0038	−104.882	−104.8836	−118.606	−118,6099
	0.00032	0.00033	0.00030	0.00031	0.00030	0.00030	0.00030	0.00031
	0.00255	0.00255	0.00240	0.00240	0.00236	0.00237	0.00238	0.00239
	0.01314	0.01314	0.01235	0.01235	0.01220	0.01220	0.01233	0.01233
	0.05195	0.05196	0.04909	0.04910	0.04844	0.04845	0.04908	0.04908
	0.15809	0.15809	0.15099	0.15099	0.14902	0.14902	0.15104	0.15105
	0.34099	0.34100	0.33176	0.33177	0.32876	0.32877	0.33177	0.33178
	0.40463	0.40463	0.40836	0.40835	0.40884	0.40884	0.40780	0.40781
	0.17114	0.17114	0.18574	0.18574	0.19018	0.19020	0.18556	0.18556
	0.01040	0.01040	0.01235	0.01235	0.01310	0.01310	0.01259	0.01260
	−0.00095	−0.00095	−0.00145	−0.00145	−0.00165	−0.00166	−0.00152	−0.00153
	0.00031	0.00031	0.00042	0.00042	0.00045	0.00045	0.00038	0.00039
	−0.00014	−0.00014	−0.00018	−0.00019	−0.00020	−0.00020	−0.00017	−0.00018
2s	−7.51002	−7.51054	−9.00301	−9.00364	−10.6060	−10.60673	−12.3208	−12.32173
	−0.00008	−0.00009	−0.00008	−0.00008	−0.00008	−0.00009	−0.00008	−0.00009
	−0.00069	−0.00069	−0.00066	−0.00066	−0.00066	−0.00066	−0.00067	−0.00067
	−0.00362	−0.00363	−0.00346	−0.00347	−0.00347	−0.00347	−0.00355	−0.00355
	−0.01440	−0.01440	−0.01382	−0.01382	−0.01384	−0.01384	−0.01422	−0.01423
	−0.04757	−0.04757	−0.04609	−0.04609	−0.04614	−0.04614	−0.04740	−0.04740
	−0.11473	−0.11471	−0.11260	−0.11258	−0.11321	−0.11320	−0.11644	−0.11642
	−0.20438	−0.20438	−0.20578	−0.20578	−0.20794	−0.20795	−0.21140	−0.21140
	−0.07669	−0.07666	−0.09047	−0.09042	−0.09603	−0.09598	−0.09415	−0.09409
	0.53543	0.53523	0.52974	0.52949	0.52772	0.52743	0.53045	0.53011
	0.58178	0.58200	0.58890	0.58917	0.59131	0.59163	0.58860	0.58898
	0.03476	0.03466	0.03739	0.03726	0.03956	0.03941	0.04085	0.04066
	−0.00872	−0.00868	−0.00861	−0.00855	−0.00833	−0.00826	−0.00785	−0.00778
3s	−0.69592	−0.69600	−0.87879	−0.87888	−1.07195	−1.07203	−1.27634	−1.27645
	0.00002	0.00002	0.00002	0.00002	0.00002	0.00003	0.00002	0.00003

	0.00019	0.00019	0.00019	0.00019	0.00020	0.00020	0.00021	0.00021
	0.00099	0.00099	0.00100	0.00100	0.00104	0.00105	0.00110	0.00111
	0.00397	0.00397	0.00404	0.00404	0.00422	0.00422	0.00448	0.00448
	0.01311	0.01311	0.01340	0.01339	0.01396	0.01395	0.01481	0.01479
	0.03239	0.03236	0.03370	0.03367	0.03541	0.03538	0.03773	0.03770
	0.05851	0.05845	0.06196	0.06189	0.06515	0.06506	0.06838	0.06828
	0.02488	0.02489	0.03162	0.03162	0.03558	0.03559	0.03699	0.03699
	−0.20193	−0.20182	−0.21687	−0.21675	−0.23035	−0.23021	−0.24463	−0.24447
	−0.36596	−0.36542	−0.38535	−0.38471	−0.39972	−0.39897	−0.40856	−0.40771
	0.61259	0.61053	0.63458	0.63227	0.64197	0.63936	0.64828	0.64539
	0.56627	0.56803	0.55752	0.55947	0.56122	0.56339	0.56446	0.56683
2*p*	−5.39985	−5.40047	−6.68128	−6.68203	−8.07086	−8.07169	−9.57015	−9.57120
	0.00370	0.00370	0.00313	0.00313	0.00294	0.00295	0.00299	0.00300
	0.02858	0.02860	0.02423	0.02425	0.02290	0.02292	0.02364	0.02366
	0.12149	0.12156	0.10600	0.10606	0.10216	0.10221	0.10589	0.10595
	0.30214	0.30222	0.28302	0.28311	0.27867	0.27878	0.28567	0.28577
	0.43369	0.43372	0.43808	0.43812	0.43849	0.43852	0.44322	0.44325
	0.29089	0.29077	0.31509	0.31496	0.31892	0.31881	0.30458	0.30445
	0.03897	0.03890	0.04567	0.04560	0.04728	0.04721	0.04162	0.04156
	−0.00423	−0.00422	−0.00430	−0.00429	−0.00378	−0.00377	−0.00368	−0.00368
	0.00138	0.00138	0.00177	0.00177	0.00195	0.00195	0.00116	0.00116
3*p*	−0.39125	−0.39145	−0.43673	−0.43697	−0.50558	−0.50584	−0.59016	−0.59049
	−0.00088	−0.00088	−0.00080	−0.00080	−0.00080	−0.00080	−0.00084	−0.00084
	−0.00682	−0.00683	−0.00619	−0.00620	−0.00618	−0.00619	−0.00662	−0.00663
	−0.03000	−0.03003	−0.02806	−0.02808	−0.02864	−0.02867	−0.03088	−0.03090
	−0.07568	−0.07572	−0.07600	−0.07604	−0.07927	−0.07931	−0.08458	−0.08462
	−0.11780	−0.11785	−0.12805	−0.12809	−0.13676	−0.13681	−0.14528	−0.14533
	−0.06422	−0.06416	−0.07442	−0.07434	−0.07645	−0.07637	−0.06726	−0.06715
	0.26816	0.26841	0.27867	0.27891	0.29440	0.29463	0.32467	0.32490
	0.56239	0.56251	0.55806	0.55816	0.55450	0.55458	0.55074	0.55079
	0.31943	0.31904	0.32395	0.32361	0.31609	0.31576	0.28994	0.28963

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[a] Ref. [7].

discrepancies observed are caused by round-off errors or other differences in precision in the two independent sets of calculations.

Differences between corresponding orbital energies are about an order of magnitude larger in general but this situation is again consistent with previous experience with numerical precision for calculations of this type. The agreement worsens slightly with increasing nuclear charge of the atom but even for argon it is quite good. Differences between corresponding SCF expansion coefficients are also relatively small, almost always less than 2.0×10^{-4}.

It is also found that these results are only very slightly dependent on the choice of lobe separations. Variations of a given lobe separation in the region of 10 to 20% of the original value for all p functions of both Al and Ar basis sets fails to alter the respective total energy values by more than 1.0×10^{-5} hartree in any case. Variations of 50–100% produce energy changes which are slightly greater than this threshhold value in a few instances but in all these cases the energy is observed to increase. No attempt has been made to simultaneously alter *all* lobe separations for a given atom by varying the lobe constant c for these AO basis sets.

3. Comparison of Grouped Gaussian Basis Sets

For molecular calculations it is convenient to form basis functions which are fixed linear combinations of primitive gaussians. Thus it seems desirable to carry out a similar comparison of cartesian and lobe function gaussians for basis sets composed of functions of this type. The recently reported second-row cartesian gaussian basis set of Huzinaga [8] is chosen for this purpose, again using the same exponents and the same relationship between lobe separation and exponent ($c = 0.03$) to construct the analogous lobe function basis. The resulting total energies are compared in Table 3 and the corresponding SCF coefficients and orbital energies are contained in Table 4.

For the most part the discrepancies in total energies between the two sets of calculations employing the grouped basis sets are still quite small, albeit somewhat larger than those obtained using Veillard's primitive gaussian functions.

Table 3. *Comparison of total energies for the atoms* Na *through* Ar *obtained from cartesian and lobe function grouped gaussian basis sets using identical exponents, given by Huzinaga*

	Cartesian basis[a]	Lobe function basis
Na	−161.81733	−161.85505
Mg	−199.60095	−199.61002
Al	−241.86953	−241.86947
Si	−288.84415	−288.84405
P	−340.70360	−340.70349
S	−397.48928	−397.48923
Cl	−459.46443	−459.46445
Ar	−526.79963	−526.79964

[a] Ref. [8].

Table 4. *Orbital energies and* SCF AO *expansion coefficients for* Na *through* Ar *obtained from Huzinaga's cartesian and the corresponding lobe function grouped gaussian basis sets*

	Na(^2S)		Mg(^1S)		Al(^2P)		Si(^3P)	
	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe
1*s*	−40.492782	−40.4810	−49.001407	−49.0303	−58.498443	−58.4992	−68.808498	−68.8099
	0.09182885	0.09182	0.08694277	0.08715	0.08684048	0.08684	0.08479833	0.08480
	0.95486364	0.95485	0.95799116	0.95804	0.95826760	0.95827	0.95952351	0.95952
	0.00022117	0.00028	0.00192940	0.00022	0.00015427	0.00015	0.00014282	0.00014
	0.00010274	0.00009	−0.00018553	0.00012	0.00013136	0.00013	0.00013142	0.00013
2*s*	−2.8013012	−2.79859	−3.7668020	−3.76755	−4.9103296	−4.91072	−6.1556445	−6.15635
	−0.02250224	−0.02250	−0.02210210	−0.02207	−0.02263477	−0.02264	−0.02254670	−0.02255
	−0.28168178	−0.28172	−0.29179847	−0.29180	−0.30070647	−0.30071	−0.31015441	−0.31015
	1.0424672	1.04238	1.0446205	1.04514	1.0478445	1.04785	1.0506969	1.05070
	−0.00038983	0.00004	0.00014409	0.00005	0.00011238	0.00011	0.00009955	0.00009
3*s*	−0.18216709	−0.18212	−0.25300526	−0.25300	−0.39337661	−0.39343	−0.53978817	−0.53990
	0.00342708	0.00344	0.00431987	0.00431	0.00530077	0.00530	0.00584365	0.00584
	0.04123965	0.04144	0.05478016	0.05479	0.06739000	0.06739	0.07745707	0.07745
	−0.20163643	−0.20236	−0.26227945	−0.26237	−0.32251960	−0.32252	−0.35728907	−0.35728
	1.0187539	1.01875	1.0311761	1.03119	1.0465853	1.04659	1.0565980	1.05660
2*p*	−1.5154493	−1.51977	−2.2807174	−2.28236	−3.2184148	−3.21880	−4.2558990	−4.25660
	0.22780139	0.22842	0.23645040	0.23686	0.24669241	0.24684	0.25423498	0.25435
	0.87712374	0.87655	0.86676292	0.86649	0.85641834	0.85627	0.84854221	0.84840
					−0.00005805	0.00012	−0.00032484	−0.00003
3*p*					−0.21015516	−0.21017	−0.29708120	−0.29714
					−0.04499412	−0.04533	−0.05552616	−0.05581
					−0.16647355	−0.16752	−0.19719808	−0.19798
					1.0188758	1.01887	1.0267779	1.02677

Table 4 (continued)

	P(^4S)		S(^3P)		Cl(^2P)		Ar(^1S)	
	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe	Cartesian[a]	Lobe
1*s*	−79.965937	−79.9669	−92.000025	−92.0022	−104.88266	−104.8853	−118.60790	−118.6095
	0.08600647	0.08600	0.07648974	0.07649	0.07943247	0.07954	0.07993758	0.07994
	0.9588790	0.95859	0.96479664	0.96480	0.96281941	0.96282	0.96256350	0.96256
	0.00012348	0.00012	0.00015354	0.00015	0.00013585	0.00013	0.00010653	0.00011
	0.00012314	0.00012	0.00012727	0.00013	0.00011336	0.00011	0.00009308	0.00009
2*s*	−7.5108890	−7.51146	−9.0031766	−9.00433	−10.607594	−10.60911	−12.321699	−12.32273
	−0.2340552	−0.02341	−0.02106527	−0.02106	−0.02227899	−0.02228	−0.02266854	−0.02267
	−0.31497845	−0.31498	−0.32076641	−0.32076	−0.32550484	−0.32550	−0.33082244	−0.33081
	1.0523699	1.05237	1.0536179	1.05362	1.0554516	1.05546	1.0571754	1.05718
	0.00005236	0.00005	0.00001022	0.00001	−0.00015405	−0.00017	0.00007704	0.00006
3*s*	−0.69636446	−0.69650	−0.87913610	−0.87937	−1.0728704	−1.07326	−1.2768097	−1.27712
	0.00651004	0.00651	0.00619249	0.00619	0.00682693	0.00683	0.00719093	0.00719
	0.08417191	0.08417	0.09038884	0.09039	0.09561545	0.09561	0.09961377	0.09961
	−0.38697734	−0.38697	−0.41330615	−0.41330	−0.43450373	−0.43449	−0.46576272	−0.46575
	1.0659503	1.06595	1.0748018	1.07480	1.0822119	1.08221	1.0937562	1.09376
2*p*	−5.4014394	−5.40202	−6.6822983	−6.68346	−8.0736308	−8.07514	−9.5722950	−9.57337
	0.27393208	0.27406	0.28436830	0.28445	0.29922249	0.29924	0.30518305	0.30533
	0.83039805	0.83030	0.82070914	0.82042	0.80715645	0.80668	0.80046162	0.80037
	−0.00008535	−0.00007	−0.00093470	−0.00012	−0.00165209	−0.00008	−0.00013577	−0.00020
3*p*	−0.39172966	−0.39180	−0.43718732	−0.43735	−0.50649205	−0.50681	−0.59089248	−0.59114
	−0.06723577	−0.06729	−0.07476995	−0.07515	−0.08341338	−0.08400	−0.08911138	−0.08914
	−0.21706198	−0.21708	−0.23110323	−0.23202	−0.24091300	−0.24228	−0.25135053	−0.25122
	1.0334763	1.03347	1.039282	1.03902	1.0438663	1.04385	1.0477950	1.04778

[a] Ref. [8].

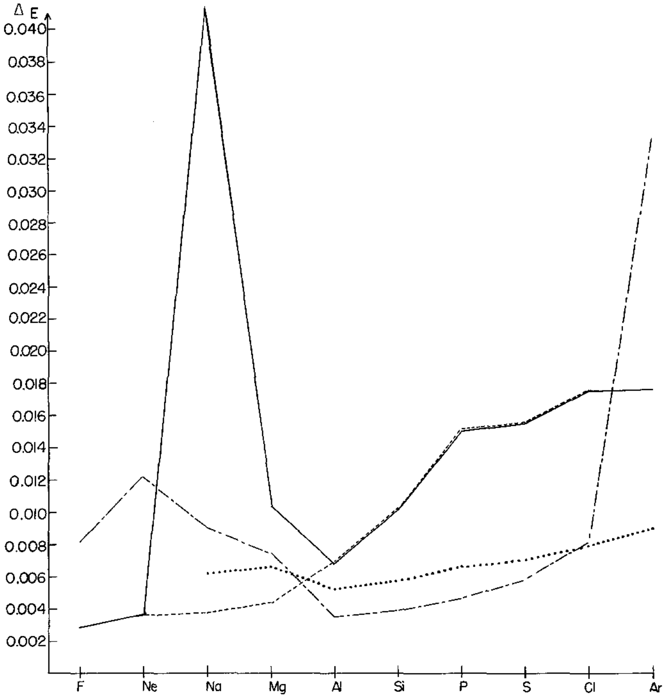

Fig. 1. Deviation of total atomic energies (hartrees) for F through Ar from the corresponding Hartree-Fock values [9] for several calculations: — — — Double Zeta [9], ····· Veillard Single Gaussian [7], ——— Huzinaga Grouped Gaussian [8] and ------ present lobe function treatment based on Huzinaga's exponents for cartesian gaussians. The curve obtained from the lobe function calculation employing Veillard's exponents cannot be distinguished from its cartesian counterpart at the scale used in this diagram

Just as in the ungrouped case, the energy differences are seen to increase from argon to a maximum at phosphorus and then to decrease again towards sodium but it is apparent that a definite break in this pattern occurs at magnesium for these grouped basis set calculations. Examination of Fig. 1, in which the energy deviations from the respective Hartree-Fock values are plotted for various basis sets as a function of the nuclear charge of the atoms, suggests quite strongly that these large discrepancies for Na and Mg (particularly for Na) cannot plausibly be attributed to any inherent distinction between the two types of functions, but rather to an error in the cartesian gaussian calculations. The close agreement between corresponding total energies is restored for Ne and F.

If the Na and Mg results are ignored for the moment it is found that the fixed group basis set calculations also show comparable but slightly worse agreement between corresponding orbital energies and SCF coefficients of lobe function and cartesian gaussian representations (Table 4) relative to the ungrouped case. It is not surprising that the discrepancies might tend to be greater for the grouped basis sets since the numerical operations associated with these calculations are expected to be carried out somewhat more precisely in the single gaussian treatment. Thus it is again concluded that the small discrepancies found to exist between the two types of gaussian atomic SCF calculations are more plausibly assigned to distinctions in numerical precision rather than in the functions themselves.

A last set of calculations dealing with variation of lobe separations in grouped basis sets remains to be discussed. In contrast to the results for primitive gaussian bases it is found that alteration of *one* lobe separation within a group (while holding all other lobe separations at their original values) may make a sizeable difference; in Na, for example, a change of 10% in the lobe separation for one of the single gaussians of Huzinaga's $\phi_{p,2}$ produces an energy *increase* of 0.009 hartree. On the other hand if *all* lobe separations are altered simultaneously by varying the lobe constant c (specifically to 0.025 and 0.035 from 0.030), and thus in a manner consistent with a scaling procedure, energy changes of less than 1.0×10^{-5} hartree are observed. It is therefore clear that the values chosen for lobe separations are much more critical for grouped basis sets, most likely because in the ungrouped calculations the SCF procedure is much less restricted in compensating for such deficiencies. By maintaining a constant value for c, however, this difference between single and grouped gaussian lobe function calculations is removed.

4. Summary and Conclusions

In summary then excellent agreement is obtained between SCF calculations using cartesian gaussian basis sets and those employing lobe functions, when identical sets of exponents are taken and lobe separations are assumed to be inversely proportional to the square roots of the corresponding exponents. This agreement can be proven to be exact in the limit of a zero constant of proportionality c; the present calculations indicate that it is also quite good (total energy discrepancies of considerably less than 1.0×10^{-4} hartree) if c is chosen to be as high as 0.03.

Of course it would be overly optimistic to conclude solely on the basis of these energy comparisons that the two types of gaussians are equivalent in practice for all applications but at the same time is seems safe to state that significant differences in calculated results for the two types of functions can arise only in cases for which the charge distribution relatively well removed from the nuclei of a given system is an important factor, since near the origin of a p orbital, cartesian and lobe function gaussians are almost analytically equivalent. In any event the atomic SCF calculations discussed herein indicate quite strongly that potential surfaces calculated using the two types of gaussians for an equivalent basis set are for all practical purposes indistinguishable[1].

Certainly one area in which advantage can be taken of the foregoing comparison of gaussian functions is that of basis set optimization. Hitherto cartesian basis sets have generally utilized different groups of exponents than those of a comparable lobe function basis but the results of the present study indicate

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[1] The specific effects of the slightly different angular characteristics of the lobe function upon calculated one-electron properties have been investigated by Harrison [10].

unequivocally that the set of exponents obtained for one type of gaussian will work equally well for the other. This correspondence should also hold for higher spherical harmonic terms since these functions can be directly related to appropriate products of *p*-type species. These considerations lead to the conclusion that the lobe function should not be considered as a fundamentally different object than the cartesian gaussian but rather simply as a convenient calculative device capable of obtaining accurate values for necessary integrals. Alternatively for molecular potentials, in which case spherical transformation properties are no longer essential by virtue of the reduced symmetry, the lobe function assumes equal status with the spherical harmonic gaussian as an immensely practical tool for carrying out *a priori* calculations for chemically interesting systems.

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Note Added in Proof: Since submitting this paper Prof. Huzinaga has informed us that the SCF results for Na and Mg reported in Ref. [8] are in error and that the corrected data are in good agreement with the gaussian lobe function results reported in the present article.

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