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Medium-size Gaussian basis sets for hydrogen through argon

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Summary. Medium-sized Gaussian basis sets are reoptimized for the ground states of the atoms from hydrogen through argon. The composition of these basis sets is (4*s*), (5*s*), and (6*s*) for H and He, (9*s*5*p*) and (12*s*7*p*) for the atoms Li to Ne, and (12*s*8*p*) and (12*s*9*p*) for the atoms Na to Ar. Basis sets for the ^2P states of Li and Na, and the ^3P states of Be and Mg are also constructed since they are useful in molecular calculations. In all cases, our energies are lower than those obtained previously with Gaussian basis sets of the same size.

Key words: Gaussian basis sets – First-row atoms – Second-row atoms – Hydrogen – Helium

1 Introduction

The overwhelming majority of contemporary quantum chemical calculations use basis sets of Gaussian-type functions (GTF). There are two compendia [1, 2] and many good reviews [3–8] on GTF basis sets. Some of the most popular medium-sized basis sets are contractions [3, 9, 10] of the variationally optimized sets of Huzinaga [11, 12]. These include his (*ns*), $n = 4, 5, 6$, sets for the hydrogen and helium atoms [11], his (9*s*5*p*) bases for Li through Ne [11], and his (12*s*8*p*) and (12*s*9*p*) sets for Na through Ar [12]. Reoptimized versions of these basis sets for H to Ne, and larger (12*s*7*p*) sets for Li to Ne, were tabulated [13] and contracted [14] by van Duijneveldt; these have also been widely used.

In this note, we report variational reoptimizations of all the basis sets explicitly mentioned above. Small improvements in the atomic energies, and nontrivial changes in the GTF exponents are found. Basis sets for the ^2P states of Li and Na, and the ^3P states of Be and Mg are also constructed for use in molecular studies.

2 Method

All self-consistent-field (SCF) calculations were done with a modified and corrected version of Pitzer's implementation [15] of the Roothaan–Bagus procedure [16]. We found that the program [15] has a bug in the construction of the Fock matrices in certain open-shell cases. We checked our correction against published results such as those of Huzinaga [12] and Clementi and Roetti [17], and against a different implementation [18] of the Roothaan–Bagus algorithm [16]. The optimization of the exponents was carried out with the conjugate direction algorithm of Powell [19].

3 Results and discussion

The results are summarized in Tables 1 and 2. In all cases, our energies are lower than those obtained with previous GTF basis sets of the same size [10–13, 20]. Our (9*s*5*p*) and (12*s*7*p*) basis sets for Li to Ne yield atomic energies that are lower than the previous best ones of van Duijneveldt [13] by amounts ranging from 6.1×10^{-6} to 1.5×10^{-4} E_H. Our (12*s*8*p*) and (12*s*9*p*) basis sets for Na to Ar yield atomic energies that are lower than the corresponding results of Huzinaga [12] by amounts between 3.1×10^{-4} and 3.4×10^{-3} E_H. These energy

Table 1. SCF energies (E) for the reoptimized basis sets for H to Ne. ΔE is the difference between the SCF and the numerical Hartree–Fock (HF) total energies. $\Delta\epsilon$ is the mean absolute difference between the SCF and numerical HF orbital energies

Basis	Atom	E/E_H	$\Delta E/mE_H$	$\Delta\epsilon/mE_H$
4*s*	H (^2S)	−0.49927841	0.72	0.72
	He (^1S)	−2.8551605	6.52	3.81
5*s*	H (^2S)	−0.49980983	0.19	0.19
	He (^1S)	−2.8598954	1.78	1.09
6*s*	H (^2S)	−0.49994557	0.05	0.05
	He (^1S)	−2.8611533	0.53	0.33
9*s*5*p*	Li (^2S)	−7.4324201	0.31	0.12
	Li (^2P)	−8.3649823	0.09	0.04
	Be (^1S)	−14.572338	0.69	0.29
	Be (^3P)	−14.510815	0.69	0.20
	B (^2P)	−24.527546	1.52	0.59
	C (^3P)	−37.685700	2.92	1.03
	N (^4S)	−54.395885	5.05	1.62
	O (^3P)	−74.800995	8.40	2.61
	F (^2P)	−99.396402	12.95	3.79
	Ne (^1S)	−128.52827	18.83	5.16
12*s*7*p*	Li (^2S)	−7.4326957	0.03	0.02
	Li (^2P)	−7.3650641	0.01	0.00
	Be (^1S)	−14.572968	0.06	0.03
	Be (^3P)	−14.511444	0.06	0.02
	B (^2P)	−24.528953	0.11	0.04
	C (^3P)	−37.688423	0.20	0.07
	N (^4S)	−54.400603	0.33	0.12
	O (^3P)	−74.808846	0.55	0.20
	F (^2P)	−99.408492	0.86	0.31
	Ne (^1S)	−128.54584	1.26	0.43

Table 2. SCF energies (E) for the reoptimized basis sets for Na to Ar. ΔE is the difference between the SCF and the numerical Hartree–Fock (HF) total energies. $\Delta\epsilon$ is the mean absolute difference between the SCF and numerical HF orbital energies

Basis	Atom	E/E_H	$\Delta E/mE_H$	$\Delta\epsilon/mE_H$
$12s8p$	Na (^2S)	−161.85585	3.06	0.75
	Na (^2P)	−161.78308	3.33	1.04
	Mg (^1S)	−199.61140	3.23	0.88
	Mg (^3P)	−199.54079	5.92	1.53
	Al (^2P)	−241.87011	6.61	1.80
	Si (^3P)	−288.84640	7.97	2.21
	P (^4S)	−340.70901	9.78	2.67
	S (^3P)	−397.49232	12.60	3.57
	Cl (^2P)	−459.46683	15.26	3.91
	Ar (^1S)	−526.79987	17.64	3.97
$12s9p$	Na (^2S)	−161.85603	2.88	0.72
	Na (^2P)	−161.78513	1.28	0.38
	Mg (^1S)	−199.61160	3.03	0.84
	Mg (^3P)	−199.54284	3.87	1.04
	Al (^2P)	−241.87239	4.32	1.26
	Si (^3P)	−288.84920	5.17	1.49
	P (^4S)	−340.71286	5.92	1.42
	S (^3P)	−397.49811	6.81	1.53
	Cl (^2P)	−459.47437	7.72	1.67
	Ar (^1S)	−526.80881	8.70	1.84

improvements are rather small in the context of molecular calculations. However, the reoptimized exponents of the tight GTF differ by as much as 25% from the previous ones [10–13] and this may be of some significance for properties other than the energy, particularly those that are related to regions close to the nucleus.

Tables 1 and 2 show that the average errors in our orbital energies, measured relative to numerical Hartree–Fock values taken from Froese-Fischer [21] for the ground states and computed with a modified version of MCHF72 [22] for the excited states, are significantly smaller than the errors in the total energies. Moreover, our optimizations were carried out sufficiently thoroughly to ensure that our calculated virial ratios deviate from the exact value of -2 by less than 5×10^{-8} in all cases. We also checked each basis set to ensure that our improved energy was not obtained by changing a GTF localized in the valence region to one in the core. Thus, we are confident that our reoptimization has not led to any imbalance in the basis sets.

Let us number the GTF exponents (α) of a given symmetry (s or p) in a given basis set such that $\alpha_1 > \alpha_2 > \cdots > \alpha_n$. Then we note that the minimum value of the ratio α_i/α_{i+1} is greater than 2.2 in each of our basis sets except the ($12s7p$) set for Li(^2S) where it is 2.0. These ratios reassure us that there will be no near-linear-dependence problems with our basis sets.

We also note that the exponent ratios of our tightest s-type GTF are almost independent of basis set size and atom in agreement with the observations of Partridge [23, 24]. Moreover, the values of these ratios are very close to those found by Partridge [23, 24] using larger basis sets. In particular, we note that

$\alpha_1/\alpha_2 = 6.67$, $\alpha_2/\alpha_3 = 4.39$, $\alpha_3/\alpha_4 = 3.53$ for the s-GTF in each of our basis sets for all the atoms from Li to Ar.

Finally, we note that all the basis sets are available via electronic mail by request to AJIT@UNB.CA. Those without access to electronic mail may request printed tables from either author.

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