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Contracted gaussian basis sets for sodium through to argon

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Abstract

Segmented [6s4p] and [6s5p] contractions of Koga and Thakkar's reoptimized (12s8p) and (12s9p) gaussian basis sets, respectively, are reported for the atoms Na through to Ar. These basis sets yield lower atomic energies than the McLean–Chandler basis sets of the same size. The basis sets are tested by performing self-consistent field geometry optimizations on NaH, MgH_2, Al_2Cl_6, SiH_4, P_2H_4, H_2S_2, SO_3, HCl and ClF_3.

Introduction

Most contemporary quantum chemical calculations use basis sets of gaussian-type functions (GTFs). There are many good reviews and compendia [1–9] of GTF basis sets. McLean and Chandler's double zeta [6s4p] and [6s5p] contractions [10] of the (12s8p) and (12s9p) GTF sets of Huzinaga [11] are among the most popular basis sets for the second row atoms from Na through to Ar.

Recently, Koga and Thakkar [12] and Schafer et al. [13] have obtained variational (12s8p) and (12s9p) GTF sets for Na to Ar that yield atomic energies lower than those of Huzinaga [11] by amounts ranging from 3.1×10^{-4} to 3.4×10^{-3} E_h. Since the reoptimized [12] exponents of the tight GTF differ by as much as 25% from the previous ones [11], this may be of some significance for properties other than the energy, particularly those that are related to regions close to the nucleus. We report segmented double zeta contractions of Koga and Thakkar's basis sets [12] for use in molecular calculations. The new basis sets are tested on atomic energies, and geometries and dipole moments of nine molecules. Hartree atomic units are used except where explicitly stated otherwise.

Contraction of the basis sets

We have used segmented [14] rather than generalized [15] contractions because many popular integral programs do not have the capability to use the latter efficiently. In segmented contractions [14], primitive GTFs, with the possible exception of one or two crucial ones, appear in only one contracted gaussian-type function (CGTF). Ideally, the contraction coefficients, the exponents and the grouping pattern should be variationally optimized simultaneously. We are not aware of any such work. Segmented CGTF basis sets with both exponents and contraction coefficients variationally optimized for a predetermined contraction pattern can be found in Ref. 16, for example. More common are segmented basis sets in which the contraction pattern (splitting) is optimized by trial and error, and the contraction coefficients are either taken from atomic calculations in the parent set as in Ref. 14, or variationally optimized as in Ref. 10.

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In this work, we examined up to 29 contraction patterns for each basis set, with the use of 0, 1 and 2 primitive GTFs appearing in two CGTF. For each pattern, the contraction coefficients were variationally optimized to minimize the spin-restricted Roothaan–Hartree–Fock (RHF) atomic energy [17]. The contraction pattern leading to the lowest energy was chosen with no attempt to impose a uniform pattern for all second-row atoms. All atomic self-consistent field (SCF) calculations were done with the ATOM program [18] modified to allow the optimization of contraction coefficients by the conjugate direction algorithm of Powell [19].

Ground state sodium and magnesium have only an *s*-type atomic orbital (AO) occupied in the valence shell, but valence *p*-type AOs are needed for molecular calculations. Hence, the basis set for magnesium was prepared by contracting the wavefunction [12] for the $1s^2 2s^2 2p^6 3s3p$ (^3P) state. The procedure for sodium was more subtle. The exponents and the contraction patterns of the s-GTF and p-GTF were obtained by contracting the wavefunctions [12] for the ground $1s^2 2s^2 2p^6 3s$ (^2S) and excited $1s^2 2s^2 2p^6 3p$ (^2P) states respectively. The contraction coefficients of this mixed basis set were then optimized for the ^2P state.

Recommended basis sets

Table 1 lists atomic RHF energies predicted by five different [6s4p] contractions of the Koga–Thakkar (KT) (12s8p) set [12], by the McLean–Chandler (MC) [6s4p] basis set denoted MC64 [10], and by the uncontracted KT (12s8p) set. The B0 contraction has no repeated GTF, whereas B1s, B1p, B1s1p and B2s respectively contain one repeated s-GTF, one repeated p-GTF, one repeated s-GTF with one repeated p-GTF, and two repeated s-GTFs. Recall that the MC contractions have one repeated s-GTF for Na, Mg and Al, but one repeated s-GTF and one repeated p-GTF for the atoms from Si through to Ar. Figure 1 and Table 1 show that B0 loses too much energy, and that B1s is always better than B1p. Except for Na, the KT contraction with the same number and type of repeated GTFs has a lower energy than the corresponding MC contraction.

The contractions that yield the lowest energy are B2s for Na to Al, and B1s1p for Si through to Ar. These basis sets have energies higher than the uncontracted ones by amounts ranging from 1.4×10^{-4} E_h to 4.24×10^{-3} E_h. These energy losses due to contraction are at least four times smaller than the errors in the uncontracted energies relative to the Hartree–Fock limit [12,20].

Table 1
Atomic energies, with signs reversed, from various GTF basis sets[a]

	B0	B1s	B1p	MC[b]	B1s1p	B2s	(12s8p)
Na(^{2}P)	161.76566	161.77166	161.76566	161.772812	161.77166	161.78011	161.78075
Mg(^{3}P)	199.53431	199.54005	199.53435	199.538028	199.54009	199.54065	199.54079
Al(^{2}P)	241.86349	241.86941	241.86367	241.867108	241.86959	241.86985	241.87011
Si(^{3}P)	288.83957	288.84490	288.84030	288.844078	288.84563	288.84559	288.84640
P(^{4}S)	340.70098	340.70597	340.70271	340.706964	340.70770	340.70691	340.70901
S(^{3}P)	397.48185	397.48682	397.48532	397.489938	397.49029	397.48808	397.49232
Cl(^{2}P)	459.45432	459.45944	459.45877	459.463266	459.46389	459.46136	459.46683
Ar(^{1}S)	526.78616	526.79155	526.79024	526.794814	526.79563	526.79419	526.79987

[a] MC is McLean and Chandler's (12s8p)/[6s4p] basis set [10]. B0, B1s, B1p, B1s1p and B2s, respectively, are [6s4p] contractions of Koga and Thakkar's (12s8p) set [12] using 0, one repeated s, one repeated p, one repeated s with one repeated p, and two repeated s primitives. (12s8p) is the uncontracted set from Ref. 12

[b] The MC contraction scheme has one repeated s primitive for Na, Mg and Al, and one repeated s primitive with one repeated p primitive for Si through to Ar.

Table 2
Atomic energies, with signs reversed, from various GTF basis sets[a]

	C0	C1s	C1p	MC[b]	C1s1p	C2s	(12s9p)
Na(^{2}P)	161.76774	161.77372	161.76774	161.773509	161.77372	161.78217	161.78281
Mg(^{3}P)	199.53638	199.54214	199.53638	199.538645	199.54214	199.54273	199.54284
Al(^{2}P)	241.86594	241.87186	241.86594	241.869933	241.87187	241.87230	241.87239
Si(^{3}P)	288.84309	288.84841	288.84309	288.847625	288.84841	288.84910	288.84920
P(^{4}S)	340.70648	340.71145	340.70656	340.711197	340.71152	340.71239	340.71286
S(^{3}P)	397.49113	397.49607	397.49113	397.496695	397.49607	397.49735	397.49811
Cl(^{2}P)	459.46633	459.47143	459.46645	459.472685	459.47155	459.47336	459.47437
Ar(^{1}S)	526.79909	526.80448	526.79974	526.806626	526.80513	526.80712	526.80881

[a] MC is McLean and Chandler's (12s9p)/[6s5p] basis set [10]. C0, C1s, C1p, C1s1p and C2s, respectively, are [6s5p] contractions of Koga and Thakkar's (12s9p) set [12] using 0, one repeated s, one repeated p, one repeated s with one repeated p, and two repeated s primitives. (12s9p) is the uncontracted set from Ref. 12

[b] The MC contraction scheme has one repeated s primitive for Na through to Si, and one repeated s primitive with one repeated p primitive for P through to Ar.

These recommended basis sets, denoted KT64, are tabulated in the Appendix.

Table 2 lists atomic RHF energies predicted by five different [6s5p] contractions of the KT (12s9p) set [12], by the MC [6s5p] basis set denoted MC65 [10], and by the uncontracted KT (12s9p) set. The C0 contraction has no repeated GTF, whereas C1s, C1p, C1s1p and C2s respectively contain one repeated s-GTF, one repeated p-GTF, one repeated s-GTF with one repeated p-GTF, and two repeated s-GTFs. Recall that the MC contractions have one repeated s-GTF for Na through to Si, but one repeated s-GTF and one repeated p-GTF for the atoms P through to Ar.

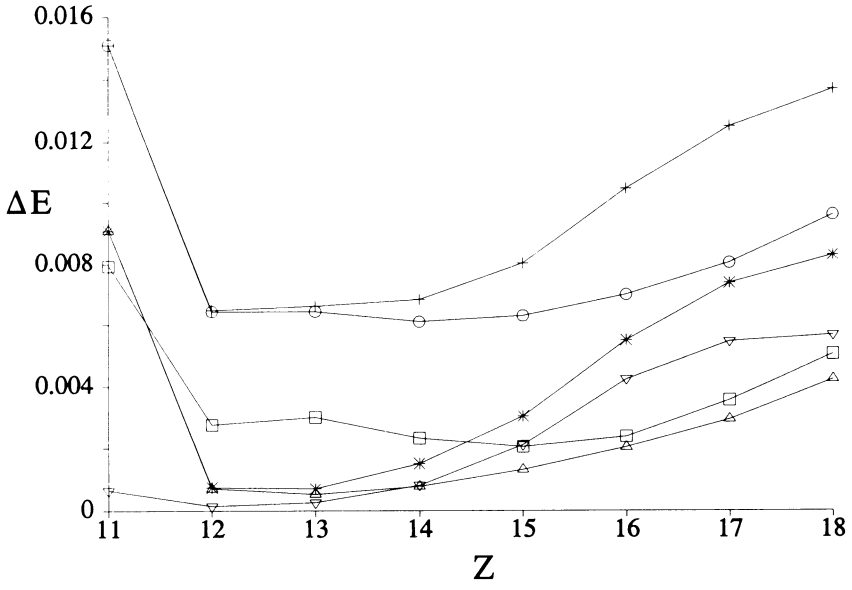

Fig. 1. ΔE is the RHF energy difference between various [6s4p] basis sets and the uncontracted (12s8p) set from Ref. 12. B0 (+), B1s (*), B1p (○), B2s (▽), MC (□), and B1s1p (△).

Figure 2 and Table 2 show that C0 loses too much energy, and that C1s is always better than C1p. Except for S, Cl and Ar, the KT contraction with the same number and type of repeated GTF is better than the corresponding MC contraction.

The C2s contractions yield the lowest energy for all the atoms from Na through to Ar. These sets have energies higher than the uncontracted ones by amounts ranging from 9.0×10^{-5} E_h to 1.69×10^{-3} E_h. These energy losses due to contraction are at least five times smaller than the errors in the uncontracted energies relative to the Hartree–Fock limit [12, 20]. These recommended basis sets, denoted KT65, are tabulated in the Appendix. Note that the contraction pattern is not uniform across the row.

Polarization functions are essential for molecular calculations. Exponents of one or two sets of polarization d-GTF from Andzelm et al. [3] are tabulated in the appendix with the correlation consistent polarization d-GTF of Dunning [21]. Ahlrichs and Taylor's formula [2] was used for the Na and Mg d-GTFs.

Molecular tests

As a test of these new basis sets, SCF geometry optimizations were performed with GAUSSIAN 90 [22] on NaH and HCl in $C_{\infty v}$ symmetry, MgH_2 in $D_{\infty h}$ symmetry, SiH_4 in T_d symmetry, SO_3 in D_{3h} symmetry, ClF_3 in C_{2v} symmetry, Al_2Cl_6 in D_{2h} symmetry, and P_2H_4 and H_2S_2 in C_2 symmetry. Each calculation was repeated in eight basis sets formed by combining the MC64, MC65, KT64 and KT65 sets with one or two polarization functions (P or 2P) as described above. For the H, O and F atoms, polarization functions were taken from Ref. 1, and double zeta basis sets from Dunning [14] and Thakkar et al. [23] respectively for use with the MC and KT basis sets.

The KT basis sets predicted total energies, at both the experimental and SCF equilibrium geometries, lower than their corresponding MC counterparts did in every case except Al_2Cl_6 for which MC64 + 2P gave a lower energy than KT64 + 2P. Tables 3 and 4 compare the SCF equilibrium geometries and dipole moments with experiment [24–27]. The differences between the

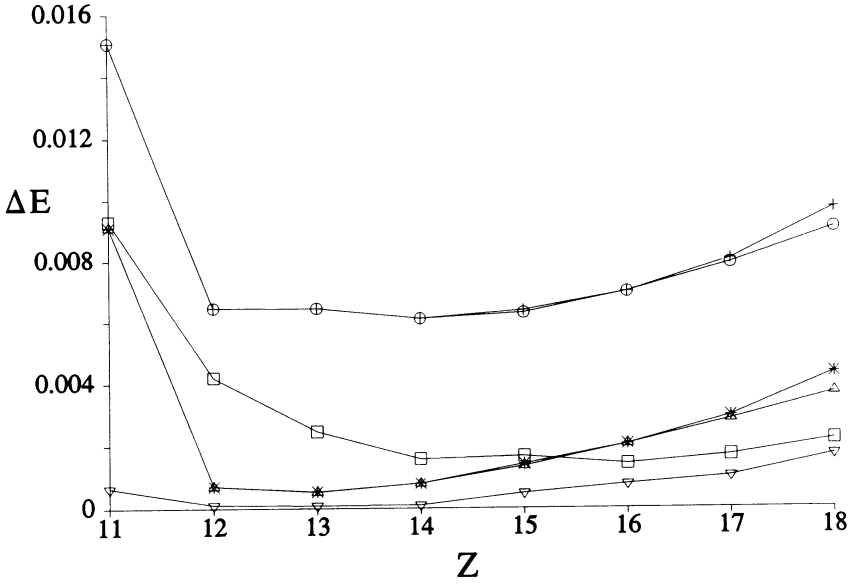

Fig. 2. ΔE is the RHF energy difference between various [6s5p] basis sets and the uncontracted (12s9p) set from Ref. 12. C0 (+), C1s (*), C1p (○), C2s (▽), MC (□), and C1s1p (△).

predictions of corresponding KT and MC basis sets of the same size are very small. There is also little difference between the geometries and dipole moments predicted by [6s4p] and corresponding [6s5p] sets. The addition of a second polarization function generally moves the calculated geometry away from experiment by a small amount. However, the second polarization function lowers the dipole moment by about 0.2 D and brings it into closer agreement with experiment.

We hope the KT64 and KT65 basis sets and our first-row sets [23] will be generally useful to the quantum chemistry community.

Table 3
SCF equilibrium geometries and dipole moments μ for HCl, NaH, SiH_4, MgH_2, SO_3, ClF_3 and Al_2Cl_6[a]

	HCl		NaH		SiH_4	MgH_2
	r(HCl)	μ(HCl)	r(NaH)	μ(NaH)	r(SiH)	r(MgH)
MC64+P	1.2733	1.3999	1.9046	6.7837	1.4827	1.7076
KT64+P	1.2746	1.4041	1.9057	6.7902	1.4836	1.7090
MC65+P	1.2746	1.4024	1.9044	6.8015	1.4819	1.7055
KT65+P	1.2746	1.4026	1.9038	6.7833	1.4829	1.7058
MC64+2P	1.2687	1.1895			1.4789	
KT64+2P	1.2695	1.1991			1.4795	
MC65+2P	1.2685	1.2045			1.4787	
KT65+2P	1.2686	1.2044			1.4791	
Expt.	1.2746	1.0929	1.8874	6.4	1.4811	

	ClF_3				SO_3
	$r(ClF_a)$	$r(ClF_b)$	$\angle(F_aClF_b)$	$\mu(ClF_3)$	r(SO)
MC64+P	1.6977	1.5886	86.57	0.9419	1.4239
KT64+P	1.7001	1.5909	86.59	0.9466	1.4246
MC65+P	1.7053	1.5930	86.58	0.9286	1.4226
KT65+P	1.7057	1.5939	86.59	0.9363	1.4231
MC64+2P	1.6788	1.5653	86.64	0.7379	1.4067
KT64+2P	1.6817	1.5680	86.65	0.7319	1.4076
MC65+2P	1.6836	1.5690	86.61	0.7297	1.4044
KT65+2P	1.6847	1.5701	86.64	0.7270	1.4051
Expt.	1.698	1.598	87.5	0.51	1.4175

	Al_2Cl_6				
	r(AlAl)	$r(AlCl_t)$	$r(AlCl_b)$	$\angle Cl_tAlCl_t$	$\angle Cl_bAlCl_b$
MC64+P	3.3032	2.0989	2.3179	123.10	89.12
KT64+P	3.2955	2.1014	2.3153	122.57	89.26
MC65+P	3.2740	2.0959	2.3036	122.54	89.43
KT65+P	3.2771	2.0988	2.3060	122.38	89.44
MC64+2P	3.2571	2.0887	2.2964	121.54	89.66
KT64+2P	3.2513	2.0899	2.2954	121.42	89.82
MC65+2P	3.2461	2.0869	2.2909	121.46	89.78
KT65+2P	3.2430	2.0900	2.2918	121.34	89.93
Expt.	3.08	2.04	2.24	122.	87.

[a] Bond lengths (r) are in ångstroms, bond angles in degrees and dipole moments in debyes. The bridging and terminal chlorines in Al_2Cl_6 are denoted Cl_b and Cl_t respectively. Experimental data is from Refs. 24 to 27

Table 4
SCF equilibrium geometries and dipole moments μ for H_2S_2 and P_2H_4

	H_2S_2				
	r(SS)	r(SH)	∠HSS	β	$\mu(H_2S_2)$
MC64 + P	2.0936	1.3376	98.06	90.15	1.4271
KT64 + P	2.0926	1.3379	98.15	90.05	1.4301
MC65 + P	2.0962	1.3373	98.19	89.80	1.4624
KT65 + P	2.0946	1.3376	98.22	89.79	1.4518
MC64 + 2P	2.0683	1.3332	98.37	89.97	1.2370
KT64 + 2P	2.0699	1.3334	98.42	90.55	1.2407
MC65 + 2P	2.0792	1.3314	98.30	89.90	1.2784
KT65 + 2P	2.0780	1.3317	98.35	89.88	1.2741
Expt.	2.055	1.327	91.3	90.6	1.18

	P_2H_4							
	r(PP)	$r(PH_a)$	$r(PH_b)$	$\angle H_aPH_b$	$\angle H_aPP$	$\angle H_bPP$	$\beta(H_aPPH_b)$	$\mu(P_2H_4)$
MC64 + P	2.2466	1.4129	1.4128	95.45	95.79	99.94	77.56	1.2618
KT64 + P	2.2450	1.4132	1.4131	95.51	95.92	100.11	77.45	1.2718
MC65 + P	2.2467	1.4123	1.4122	95.69	96.07	100.33	77.33	1.3486
KT65 + P	2.2434	1.4128	1.4128	95.65	96.11	100.36	77.30	1.3206
MC64 + 2P	2.2231	1.4084	1.4078	95.54	95.93	100.36	77.34	1.0896
KT64 + 2P	2.2237	1.4086	1.4081	95.58	96.04	100.46	77.44	1.1029
MC65 + 2P	2.2294	1.4069	1.4065	95.71	96.13	100.51	77.69	1.1520
KT65 + 2P	2.2279	1.4073	1.4068	95.66	96.15	100.53	77.75	1.1424
Expt.	2.219	1.414	1.417	92.	94.3	99.1	74.	

[a] Bond lengths are in ångströms, angles in degrees and dipole moments in debyes. β is a dihedral angle. The hydrogens on each P in diphosphine are nonequivalent and are denoted by H_a and H_b respectively. Experimental data is from Refs. 25 and 26

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Appendix

Tables A1 and A2 list the exponents (α) and contraction coefficients (c) of the recommended (12s8p)/[6s4p] CGTF basis sets for Na through to Si, and P through to Ar respectively. Tables A3 and A4 list the exponents (α) and contraction coefficientions (c) of the recommended (12s9p)/[6s5p] CGTF basis sets for Na through to Si, and P through to Ar respectively. Table A5 lists various exponents of polarization functions that can be used with these basis sets.

Table A1
Exponents (α) and contraction coefficients (c) of the (12s8p)/[6s4p] CGTF basis sets for Na, Mg, Al and Si (dashed lines separate the contracted functions)[a]

	Na		Mg		Al		Si	
	α	c	α	c	α	c	α	c
s	3.1747(+4)	0.000555	4.8789(+4)	0.000622	6.4651(+4)	0.000729	7.9916(+4)	0.000662
	4.7610(+3)	0.004296	7.3150(+3)	0.004817	9.6928(+3)	0.005650	1.1981(+4)	0.005136
	1.0835(+3)	0.022119	1.6650(+3)	0.024934	2.2062(+3)	0.029297	2.7270(+3)	0.026641
	3.0655(+2)	0.087069	4.7139(+2)	0.099638	6.2480(+2)	0.117830	7.7232(+2)	0.107614
	9.9535(+1)	0.259153	1.5353(+2)	0.274441	2.0369(+2)	0.331827	2.5185(+2)	0.342984
	3.5411(+1)	0.338828	5.5126(+1)	0.524895	7.3362(+1)	0.616998	9.0773(+1)	0.614486
	4.3863	0.560707	8.7023(00)	0.272209		-------		-------
		-------		-------	2.0369(+2)	0.022861	9.0773(+1)	0.105477
	3.5411(+1)	0.412718	1.5353(+2)	0.036570	7.3362(+1)	0.130180	3.5378(+1)	0.627405
	1.3295(+1)	1.126238	5.5126(+1)	0.158410	2.8579(+1)	0.625818	1.4515(+1)	0.316660
	4.3863	−1.202085	2.1339(+1)	0.839856	1.1761(+1)	0.282298		-------
		-------		-------		-------		
	1.6744	1.000000	2.5736	1.000000	3.3004	1.000000	4.0546	1.000000
		-------		-------		-------		-------
	5.8851(−1)	1.000000	8.8816(−1)	1.0000000	1.1725	1.000000	1.4821	1.000000
		-------		-------		-------		-------
	5.6403(−2)	1.000000	1.1336(−1)	1.000000	1.7530(−1)	1.000000	2.5184(−1)	1.000000
		-------		-------		-------		-------
	2.3068(−2)	1.000000	4.6334(−2)	1.000000	6.4772(−2)	1.000000	9.2488(−2)	1.000000
p	1.5017(+2)	0.008410	2.0475(+2)	0.007377	2.5966(+2)	0.004988	3.1686(+2)	0.004200
	3.5129(+1)	0.061145	4.8071(+1)	0.054892	6.1083(+1)	0.037633	7.4637(+1)	0.031987
	1.0913(+1)	0.244842	1.5038(+1)	0.227386	1.9193(+1)	0.158799	2.3532(+1)	0.136560
	3.8379	0.564139	5.3604	0.551369	6.8939	0.395221	8.5039	0.344695
	4.7726(−1)	0.444995	7.1520(−1)	0.473348	2.5777	0.559939	3.2224	0.626154
		-------		-------		-------		-------
							3.2224	−0.659595
	1.3749	1.000000	1.9733	1.000000	9.5835(−1)	1.000000	1.2310	1.401307
		-------		-------		-------		-------
	7.2315(−2)	1.000000	1.4500(−1)	1.000000	2.1015(−1)	1.000000	2.9689(−1)	1.000000
		-------		-------		-------		-------
	2.2089(−2)	1.000000	4.4535(−2)	1.000000	5.9953(−2)	1.000000	8.7816(−2)	1.000000

[a] $A\,(\pm n)$ means $A \times 10^{\pm n}$.

Table A2
Exponents (α) and contraction coefficients (c) of the (12s8p)/[6s4p] CGTF basis sets for P, S, Cl and Ar (dashed lines separate the contracted functions)[a]

	P		S		Cl		Ar	
	α	c	α	c	α	c	α	c
s	9.5316(+4)	0.000640	1.1139(+5)	0.000625	1.2827(+5)	0.000615	1.4603(+5)	0.000608
	1.4289(+4)	0.004963	1.6699(+4)	0.004851	1.9229(+4)	0.004775	2.1891(+4)	0.004719
	3.2524(+3)	0.025754	3.8009(+3)	0.025180	4.3767(+3)	0.024785	4.9827(+3)	0.024495
	9.2111(+2)	0.104283	1.0764(+3)	0.102130	1.2395(+3)	0.100662	1.4111(+3)	0.099593
	3.0040(+2)	0.334056	3.5105(+2)	0.328375	4.0424(+2)	0.324513	4.6021(+2)	0.321716
	1.0830(+2)	0.626110	1.2657(+2)	0.633505	1.4577(+2)	0.638512	1.6597(+2)	0.642135
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	1.0830(+2)	0.091101	1.2657(+2)	0.082257	1.4577(+2)	0.076443	1.6597(+2)	0.072380
	4.2199(+1)	0.623392	4.9313(+1)	0.619993	5.6788(+1)	0.617157	6.4660(+1)	0.614707
	1.7277(+1)	0.333852	2.0166(+1)	0.345295	2.3210(+1)	0.353391	2.6425(+1)	0.359494
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	4.8575	1.000000	5.7206	1.000000	6.6442	1.000000	7.6283	1.000000
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	1.8176	1.000000	2.1822	1.000000	2.5751	1.000000	2.9959	1.000000
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	3.3738(−1)	1.000000	4.3250(−1)	1.000000	5.3643(−1)	1.000000	6.4959(−1)	1.000000
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	1.2323(−1)	1.000000	1.5685(−1)	1.000000	1.9353(−1)	1.000000	2.3340(−1)	1.000000
p	3.7051(+2)	0.004295	4.0006(+2)	0.004867	4.1866(+2)	0.005612	4.5470(+2)	0.006006
	8.7337(+1)	0.032869	9.4281(+1)	0.037088	9.8592(+1)	0.042465	1.0707(+2)	0.045355
	2.7598(+1)	0.140919	2.9795(+1)	0.157010	3.1120(+1)	0.176456	3.3795(+1)	0.187010
	1.0010(+1)	0.355915	1.0791(+1)	0.384802	1.1212(+1)	0.415765	1.2151(+1)	0.432214
	3.8295	0.610287	4.1322	0.568277	4.2580	0.521128	4.6008	0.494819
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	3.8295	−0.557505	4.1322	−0.382228	4.2580	−0.213357	4.6008	−0.121592
	1.4964	1.360767	1.6329	1.264558	1.6291	1.151818	1.6827	1.086377
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	3.9274(−1)	1.000000	4.7406(−1)	1.000000	5.3376(−1)	1.000000	5.9264(−1)	1.000000
		- - - - - - -		- - - - - - -		- - - - - - -		- - - - - - -
	1.1881(−1)	1.000000	1.4111(−1)	1.000000	1.6252(−1)	1.000000	1.8577(−1)	1.000000

[a] $A\,(\pm n)$ means $A \times 10^{\pm n}$.

Table A3
Exponents (α) and contraction coefficients (c) of the (12s9p)/[6s5p] CGTF basis sets for Na, Mg, Al and Si (dashed lines separate the contracted functions)[a]

	Na		Mg		Al		Si	
	α	c	α	c	α	c	α	c
s	3.1750(+4)	0.000551	4.8776(+4)	0.000622	6.4654(+4)	0.000729	7.9938(+4)	0.000691
	4.7614(+3)	0.004263	7.3133(+3)	0.004819	9.6932(+3)	0.005649	1.1984(+4)	0.005356
	1.0836(+3)	0.021949	1.6646(+3)	0.024943	2.2063(+3)	0.029296	2.7278(+3)	0.027793
	3.0657(+2)	0.086403	4.7128(+2)	0.099679	6.2482(+2)	0.117827	7.7253(+2)	0.112197
	9.9543(+1)	0.257161	1.5349(+2)	0.274545	2.0370(+2)	0.331788	2.5193(+2)	0.312046
	1.3297(+1)	−0.918173	5.5114(+1)	0.524866	7.3367(+1)	0.617037	9.0801(+1)	0.641269
	4.3876	1.534983	8.6995	0.272076		-------		-------
		-------		-------	2.0370(+2)	0.022868	2.5193(+2)	0.024660
	3.5415(+1)	0.412651	1.5349(+2)	0.036559	7.3367(+1)	0.130128	9.0801(+1)	0.103686
	1.3297(+1)	1.126652	5.5114(+1)	0.158550	2.8581(+1)	0.625828	3.5388(+1)	0.619547
	4.3876	−1.201241	2.1334(+1)	0.839736	1.1761(+1)	0.282335	1.4518(+1)	0.312594
		-------		-------		-------		-------
	1.6747	1.000000	2.5735	1.000000	3.3007	1.000000	4.0555	1.000000
		-------		-------		-------		-------
	5.8860(−1)	1.000000	8.8812(−1)	1.000000	1.1727	1.000000	1.4824	1.000000
		-------		-------		-------		-------
	5.6403(−2)	1.000000	1.1308(−1)	1.000000	1.7516(−1)	1.000000	2.5155(−1)	1.000000
		-------		-------		-------		-------
	2.3069(−2)	1.000000	4.6164(−2)	1.000000	6.4712(−2)	1.000000	9.2376(−2)	1.000000
p	2.6476(+2)	0.003397	3.5695(+2)	0.003066	4.4191(+2)	0.002948	4.8138(+2)	0.003135
	6.2518(+1)	0.026558	8.4406(+1)	0.024379	1.0455(+2)	0.023628	1.1386(+2)	0.025035
	1.9772(+1)	0.120030	2.6828(+1)	0.112718	3.3316(+1)	0.110479	3.6270(+1)	0.116127
	7.2105	0.349520	9.8543	0.340404	1.2287(+1)	0.337743	1.3373(+1)	0.346295
	2.7922	0.630729	3.8690	0.642956	4.8600	0.646095	5.2769	0.633951
		-------		-------		-------		-------
	1.0793	1.000000	1.5361	1.000000	1.9600	1.000000	2.1346	1.000000
		-------		-------		-------		-------
	4.0513(−1)	1.000000	6.0039(−1)	1.000000	7.8444(−1)	1.000000	8.6464(−1)	1.000000
		-------		-------		-------		-------
	6.5593(−2)	1.000000	1.3239(−1)	1.000000	1.8905(−1)	1.000000	2.5412(−1)	1.000000
		-------		-------		-------		-------
	2.0688(−2)	1.000000	4.1647(−2)	1.000000	5.5679(−2)	1.000000	7.9238(−2)	1.000000

[a] $A\,(\pm n)$ means $A \times 10^{\pm n}$.

Table A4
Exponents (α) and contraction coefficients (c) of the (12s9p)/[6s5p] CGTF basis sets for P, S, Cl and Ar (dashed lines separate the contracted functions)[a]

	P		S		Cl		Ar	
	α	c	α	c	α	c	α	c
s	9.5362(+4)	0.000671	1.1144(+5)	0.000489	1.2831(+5)	0.000471	1.4605(+5)	0.000459
	1.4296(+4)	0.005201	1.6706(+4)	0.003789	1.9235(+4)	0.003653	2.1894(+4)	0.003562
	3.2539(+3)	0.026996	3.8025(+3)	0.019679	4.3780(+3)	0.018982	4.9834(+3)	0.018511
	9.2155(+2)	0.109246	1.0769(+3)	0.079724	1.2399(+3)	0.076985	1.4113(+3)	0.075133
	3.0054(+2)	0.301509	3.5122(+2)	0.256711	4.0437(+2)	0.248627	4.6029(+2)	0.243200
	1.0835(+2)	0.654053	1.2663(+2)	0.492638	1.4581(+2)	0.483583	1.6599(+2)	0.477454
		-------	4.9333(+1)	0.274191	5.6803(+1)	0.295065	6.4668(+1)	0.308976
	3.0054(+2)	0.025512		-------		-------		-------
	1.0835(+2)	0.090683	1.2663(+2)	0.102748	1.4581(+2)	0.099763	1.6599(+2)	0.097697
	4.2217(+1)	0.614733	4.9333(+1)	0.526774	5.6803(+1)	0.512345	6.4668(+1)	0.501878
	1.7283(+1)	0.329164	2.0172(+1)	0.426072	2.3215(+1)	0.443662	2.6428(+1)	0.456245
		-------		-------		-------		-------
	4.8591	1.000000	5.7223	1.000000	6.6448	1.000000	7.6278	1.000000
		-------		-------		-------		-------
	1.8182	1.000000	2.1829	1.000000	2.5754	1.000000	2.9957	1.000000
		-------		-------		-------		-------
	3.3700(−1)	1.000000	4.3252(−1)	1.000000	5.3694(−1)	1.000000	6.5030(−1)	1.000000
		-------		-------		-------		-------
	1.2310(−1)	1.000000	1.5692(−1)	1.000000	1.9377(−1)	1.000000	2.3368(−1)	1.000000
p	5.0569(+2)	0.007271	5.7200(+2)	0.004323	6.6115(+2)	0.004295	7.5961(+2)	0.004245
	1.1955(+2)	0.057687	1.3524(+2)	0.034346	1.5638(+2)	0.034282	1.7972(+2)	0.034025
	3.8032(+1)	0.264208	4.3059(+1)	0.157434	4.9857(+1)	0.158046	5.7374(+1)	0.157749
	1.3984(+1)	0.761878	1.5847(+1)	0.451717	1.8390(+1)	0.456413	2.1209(+1)	0.458871
		-------	2.4852	0.630388	2.9227	0.623234	3.4158	0.619027
	5.4720	0.565534		-------		-------		-------
	2.1836	0.495678	6.2086	1.000000	7.2374	1.000000	8.3842	1.000000
		-------		-------		-------		-------
	8.0513(−1)	1.000000	8.6994(−1)	1.000000	1.0223	1.000000	1.2058	1.000000
		-------		-------		-------		-------
	2.8905(−1)	1.000000	3.2361(−1)	1.000000	3.8214(−1)	1.000000	4.5244(−1)	1.000000
		-------		-------		-------		-------
	9.7593(−2)	1.000000	1.1023(−1)	1.000000	1.3041(−1)	1.000000	1.5488(−1)	1.000000

[a] $A\,(\pm n)$ means $A \times 10^{\pm n}$.

Table A5
Exponents of polarization (five-membered) d-GTFs[a]

	P	$2P$	P_D
Na	0.157		
Mg	0.234		
Al	0.198	(0.090, 0.328)	0.189
Si	0.262	(0.118, 0.424)	0.275
P	0.340	(0.153, 0.537)	0.373
S	0.421	(0.183, 0.659)	0.478
Cl	0.514	(0.220, 0.797)	0.600
Ar	0.617	(0.263, 0.950)	0.738

[a] The P and $2P$ sets are from Andzelm et al. [3] and P_D is from Dunning [21]