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Double- and triple-zeta Slater-type basis sets with common exponents

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Abstract. Double- and triple-zeta basis sets of Slater-type functions (STFs) are developed for the 17 atoms from He to Ar. For computational economy, the exponents of STFs corresponding to the same atomic subshell are restricted to be common. Instead, the principal quantum numbers of the STFs are thoroughly optimized within the framework of integer values to reduce the energy loss due to the common exponent restriction.

Key words: Optimized basis sets – Slater-type functions – Common exponent restriction – Hartree–Fock energies – Atoms He to Ar

1 Introduction

With the aim of improving the description of atomic electronic structure, Koga et al. [1] reoptimized the exponents, ζ, and principal quantum numbers, n, of the classical wave functions of Clementi and Roetti [2] based on Slater-type functions (STFs) and showed that the optimum choice of n improves notably the double-zeta (DZ) approximation of atoms. The new DZ functions have been referred to as improved DZ (IDZ). Within the single-zeta (SZ) framework, Koga and coworkers [3, 4] have also reported that an extension of the STF n from integers to nonintegers further improves the description of the atomic electronic state.

In previous work [5–7], we showed that the use of a single exponent, which is common to a group of some STFs, decreases significantly the integral computational time as a consequence of the reduction in the number of different exponents. They were named single-exponent STFs (SESTFs). When two and three STFs with a common exponent but smallest different integer n values are assigned to each atomic subshell, the resultant functions are called conventional DZ-SESTF (CDZ-SESTF) and conventional triple-zeta (TZ) SESTF (CTZ-SESTF), respectively. We also proposed [8] noninteger-n DZ (NDZ) basis sets which incorporate the noninteger n into the SESTF scheme. They were named NDZ-SESTF.

The increased flexibility by the use of noninteger n in STFs undoubtedly improves the quality of the basis functions; however, almost all existing molecular codes do not accept noninteger values for STF n. The purpose of this work is to construct SESTF basis sets of DZ and TZ sizes using STFs with integer n. An important point is that we optimize the integer n as well as ζ variationally in order to reduce the energy loss in the SESTF scheme, while keeping their computational efficiency. The two new sets of wave functions developed in this study will be referred to as IDZ-SESTF and ITZ-SESTF, where the acronym “I” stands for “improved”. The next section outlines our computational method, and in Sect. 3 the results are presented and compared with those from the updated CDZ [1], CDZ-SESTF, CTZ-SESTF, and NDZ-SESTF [8]. Hartree atomic units are used throughout.

2 Computational outline

We focused our examinations on the SESTF method, in which the same exponent is shared by two (DZ) and three (TZ) STFs corresponding to an atomic subshell [5], and the DZ and TZ calculations were performed for the atoms from He to Ar in their ground state within the Roothaan–Hartree–Fock (RHF) framework. All our RHF calculations were carried out using a modified and corrected version [9] of Pitzer’s program [10]. The variational optimization of the nonlinear ζ parameters was performed by the conjugate directions method [11], while the optimization of n was performed by a step grid variation allowing a maximum value of 10 for n of the atoms from He to Ne and 7 for those of the atoms from Na to Ar. For the atoms from He to Ne, we never met an optimum value of $n = 10$. In the optimization of the atoms Na to Ar, however, we found $n = 7$ is best for some STFs. In the latter cases, the maximum value allowed was increased to assure its optimality.

We tested several initial values for the nonlinear parameters in order to find the best minimum. In all our final results, the virial

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3 Results and discussion

Table 1 summarizes the RHF total energies, $E(W)$, for the ground-state atoms from He to Ar obtained from six different wave functions: W = CDZ, NDZ-SESTF, CDZ-SESTF, CTZ-SESTF, IDZ-SESTF, and ITZ-SESTF. The best energy is obtained by CDZ for seven atoms (He, Li, and O—Mg), by NDZ-SESTF for three atoms (B, C, and N), and by ITZ-SESTF for seven atoms (Be and Al—Ar). Among the four SESTF methods, we find in general that NDZ-SESTF with noninteger n gives lower energies than the other SESTFs with integer n, except for six atoms (Al to Ar), where ITZ-SESTF is the best. Within the DZ SESTF scheme with integer n, the optimization of the STF n results in a significant improvement in atomic total energies. The largest improvement, E(CDZ-SESTF) − E(IDZ-SESTF), amounts to 0.64 hartrees for the Mg atom. In the TZ SESTF scheme with integer n, however, the total energy-lowering obtained by the optimization of n is not so dramatic. Among the 17 atoms, the best improvement, E(CTZ-SESTF) − E(ITZ-SESTF), is 7 mhartrees for the Mg atom. Thus, the total energy error introduced by the SESTF scheme decreases as the number of STFs assigned for a subshell increases and is balanced with the optimization effect of n.

The total energy errors, $\Delta E(W) = E(W) - E(\mathrm{NHF})$, where $E(\mathrm{NHF})$ denotes the HF limit values obtained by the numerical HF (NHF) method [12], of the five wave functions W = CDZ, NDZ-SESTF, CTZ-SESTF, IDZ-SESTF, and ITZ-SESTF are plotted in Fig. 1. ΔE(CDZ-SESTF) is not shown since its error is considerably larger than that of the other five. This also implies that within the DZ approximation, the energy increase by the SESTF method, as seen in ΔE(CDZ-SESTF), is sufficiently compensated, as seen in ΔE(IDZ-SESTF), by the optimization of the STF n by keeping them as integers. However, the IDZ-SESTF energy errors in Fig. 1 are not still as small as the CDZ, NDZ-SESTF, CTZ-SESTF, and ITZ-SESTF ones. The use of noninteger n is required in the DZ SESTF scheme to obtain a result comparable with that from CDZ. (Notice that the number of optimized exponents in a DZ SESTF basis is equivalent to the number of exponents in an SZ basis.) In the TZ SESTF basis, however, the addition of one more STF with a common exponent to a DZ SESTF gives the total energy errors comparable with, or smaller than the, CDZ ones, albeit the number of independent exponents is exactly the same as the SZ basis.

We also examined the accuracy of the orbital energies of occupied atomic orbitals; however, the details are not given here because the results are essentially parallel to those of the total energies described previously. When the outermost orbital energies obtained with the previously mentioned six wave functions are compared with the NHF values, the differences are generally larger for CDZ-SESTF and smaller for CDZ and ITZ-SESTF. The ITZ-SESTF gives the outermost orbital energies closest to the NHF ones for the six atoms from He to Be and from Al to P, the CDZ values are closest for the ten atoms from B to Mg, S, and Cl, and the CTZ-SESTF is the best for the Ar atom.

We refer to the STFs forming an SESTF set as sk and pk for s- and p-type functions, respectively. The index k in the sk (pk) notation enumerates the s-type (p-type) STFs in a decreasing order of ζ and in an increasing order of n among two or three STFs sharing the same exponent. This numeration corresponds to the arrangement of STFs from the tightest to the most diffuse in a given symmetry. Thus, the $s1$ and $s2$ functions in DZ

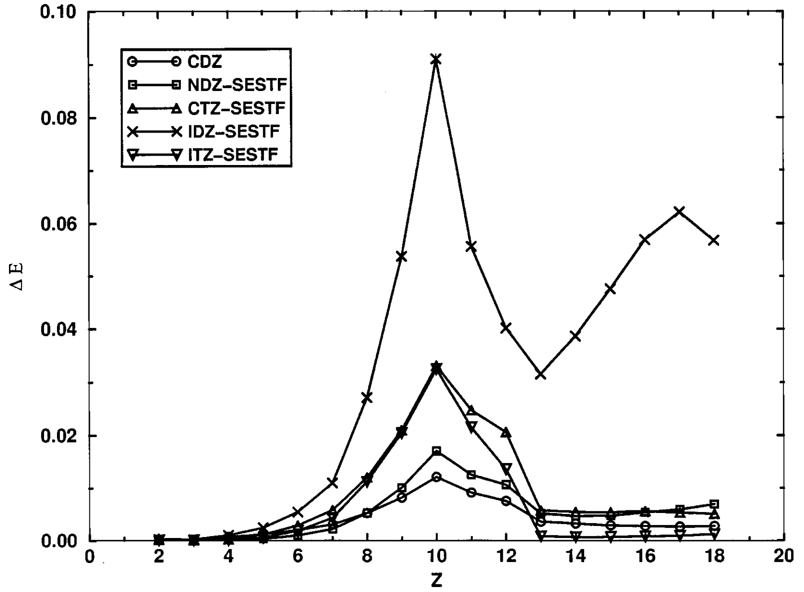
Table 1. Comparison of the six Roothaan–Hartree–Fock total energies (hartrees) for the atoms from He to Ar obtained from the wave functions conventional double zeta (*CDZ*), noninteger-*n* double zeta (*NDZ*)-single-exponent Slater-type function (*SESTF*), CDZ-SESTF, conventional triple zeta (*CTZ*)-SESTF, improved double zeta (*IDZ*)-SESTF, and improved triple zeta (*ITZ*)-SESTF

Atom	CDZ[a]	NDZ-SESTF[b]	CDZ-SESTF	CTZ-SESTF	IDZ-SESTF	ITZ-SESTF
He	−2.86167263	−2.861591066	−2.847656250	−2.861590055	−2.861470758	−2.861666717
Li	−7.43272228	−7.432711965	−7.425989357	−7.432703053	−7.432550230	−7.432716862
Be	−14.5723706	−14.57295716	−14.56522801	−14.57280356	−14.57202941	−14.57299790
B	−24.5279215	−24.52878429	−24.50948594	−24.52796510	−24.52664335	−24.52854283
C	−37.6867513	−37.68775704	−37.63709731	−37.68580336	−37.68329111	−37.68683986
N	−54.3979559	−54.39886946	−54.28828796	−54.39521618	−54.39008205	−54.39672901
O	−74.8043333	−74.80430697	−74.56565743	−74.79753895	−74.78239172	−74.79831534
F	−99.4013191	−99.39939594	−98.97438297	−99.38849830	−99.35577468	−99.38906194
Ne	−128.535120	−128.5302272	−127.8525173	−128.5141329	−128.4561906	−128.5147219
Na	−161.850044	−161.8466218	−161.1783395	−161.8344057	−161.8035422	−161.8376090
Mg	−199.607034	−199.6039206	−198.9335757	−199.5939678	−199.5744263	−199.6009875
Al	−241.873245	−241.8717395	−241.6549989	−241.8711344	−241.8452813	−241.8760329
Si	−288.851202	−288.8497821	−288.5809095	−288.8489979	−288.8157846	−288.8537971
P	−340.715991	−340.7141361	−340.4217807	−340.7134866	−340.6712766	−340.7181905
S	−397.502323	−397.4996992	−397.1740586	−397.4994388	−397.4481223	−397.5042343
Cl	−459.479636	−459.4763426	−459.1256637	−459.4769611	−459.4201199	−459.4813360
Ar	−526.815145	−526.8109392	−526.4393201	−526.8127961	−526.7610526	−526.8166793

[a] From Ref. [1]

[b] From Ref. [8]

Fig. 1. The total energy errors of the conventional double zeta (*CDZ*), noninteger-*n* double zeta (*NDZ*)-single-exponent Slater-type function(*SESTF*), improved double zeta (*IDZ*)-SESTF, conventional triple zeta (*CTZ*)-SESTF, and improved triple zeta (*ITZ*)-SESTF approximations relative to the numerical Hartree–Fock values



SESTFs and *s*1, *s*2, and *s*3 functions in TZ SESTFs, for example, are the main contributions to the 1*s* atomic orbital. Following this arrangement, the optimum *n* for the IDZ-SESTF and ITZ-SESTF wave functions are given in Table 2, in which *s*- and *p*-type functions are separated by a slash and the STFs with different ζ are distinguished by a comma. The optimum integer *n* values obtained in the IDZ-SESTF approximation compare well with the optimum noninteger *n* values obtained in the NDZ-SESTF approximation presented in Fig. 3 of Ref. [8]; however, we do not find any systematic rules for the arrangement of the optimum integer *n* values in both IDZ- and ITZ-SESTF wave functions. Nevertheless, if one wishes to use a unified arrangement of *n* throughout a period, we may propose within a DZ scheme

Li, Be	13, 37
B—Ne	13, 37/25
Na, Mg	13, 36, 12/25
Al—Ar	13, 36, 12/25, 37 .

However, this choice of the STF *n* introduces total energy errors of 2×10^{-4}, 4×10^{-4}, 7×10^{-4}, 4×10^{-3}, and 2×10^{-2} hartrees for Li, Na, Al, Cl, and Ar atoms, respectively, relative to the *E*(IDZ-SESTF). For heavier atoms, such as Ar, the error is not trivial, and we recommend using the optimum *n* values given in Table 2 for individual atoms.

Table 3 exemplifies and compares the parameters *n* and ζ of the optimum NDZ-, CDZ-, IDZ-, CTZ-, and ITZ-SESTF wave functions for the Si atom. As mentioned earlier, the integer *n* values in IDZ-SESTF better approximate the noninteger *n* values in NDZ-SESTF than those in CDZ-SESTF, if we compare the three DZ SESTF functions. There are exceptions, however. For the *p*3 and *p*4 STFs, IDZ-SESTF has *n* values far from those of NDZ-SESTF because the optimum *n* value (1.43) is smaller than the smallest nominal value (2) of *p*-type functions. The ζ parameters in Table 3 for the five SESTF wave functions are not very different, particularly for those corresponding to outer atomic orbitals.

Table 2. Optimum quantum numbers for the IDZ- and ITZ-SESTF basis sets for the atoms from He to Ar

Atom	IDZ-SESTF	ITZ-SESTF
He	13	137
Li	13, 12	123, 124
Be	13, 37	123, 125
B	13, 37/25	123, 125/247
C	13, 37/25	123, 125/247
N	13, 37/25	123, 125/247
O	13, 37/25	123, 125/247
F	13, 37/25	123, 234/234
Ne	13, 37/25	123, 125/234
Na	13, 37, 36/25	123, 235, 136/247
Mg	13, 36, 12/25	123, 235, 236/247
Al	13, 36, 12/25, 23	123, 235, 236/247, 237
Si	13, 36, 12/25, 37	123, 235, 125/247, 236
P	13, 36, 12/25, 37	123, 235, 234/247, 236
S	12, 12, 36/25, 37	123, 124, 125/247, 345
Cl	13, 36, 37/24, 24	123, 124, 236/247, 345
Ar	13, 36, 37/24, 24	123, 124, 125/247, 345

The variation of the optimum exponents in the CDZ- and IDZ-SESTF wave functions are shown as a function of the atomic number, *Z*, in Fig. 2. The results again confirm the approximate linear *Z*-dependence of exponents observed in our previous studies on SESTF basis sets, in which common exponents were optimized by either subshells or shells [6, 7] with integer or noninteger [8] STF *n*; however, some deviations from approximate linearity appear in Fig. 2. They may not be due to the sudden change in *n* from one atom to the next, since they are found in both the CDZ- and IDZ-SESTF functions. The exponent for the *s*1 and *s*2 STFs in CDZ- and IDZ-SESTF are similar, partly because the *s*1 STFs have the same value (unity) of *n*. On the other hand, the exponent for the *s*3 and *s*4 STFs is smaller for CDZ-SESTF than for IDZ-SESTF, due to larger *n* in IDZ-SESTF. This exponent in IDZ-SESTF shows a small jump when we move from $Z = 11$ to 12. The corresponding

Table 3. Comparison of the optimum SESTF parameters for the Si atom

l	*n*					*ζ*				
	NDZ	CDZ	IDZ	CTZ	ITZ	NDZ	CDZ	IDZ	CTZ	ITZ
s	1.001134	1	1	1	1					
	2.473692	2	3	2	2	14.344572	13.875341	13.942950	14.355232	15.092091
				3	3					
	2.529732	1	3	1	2					
	5.144439	2	6	2	3	6.546227	4.889653	7.396630	4.322021	5.194647
				3	5					
	0.839932	1	1	1	1					
	2.032771	2	2	2	2	1.240714	1.280011	1.251427	1.215925	1.292206
				3	5					
p	1.930847	2	2	2	2					
	4.473197	3	5	3	4	5.631067	5.538538	5.806091	5.808663	6.826391
				4	7					
	1.430353	2	3	2	2					
	2.243284	3	7	3	3	0.994952	1.769063	1.468524	1.251489	1.338038
				4	6					

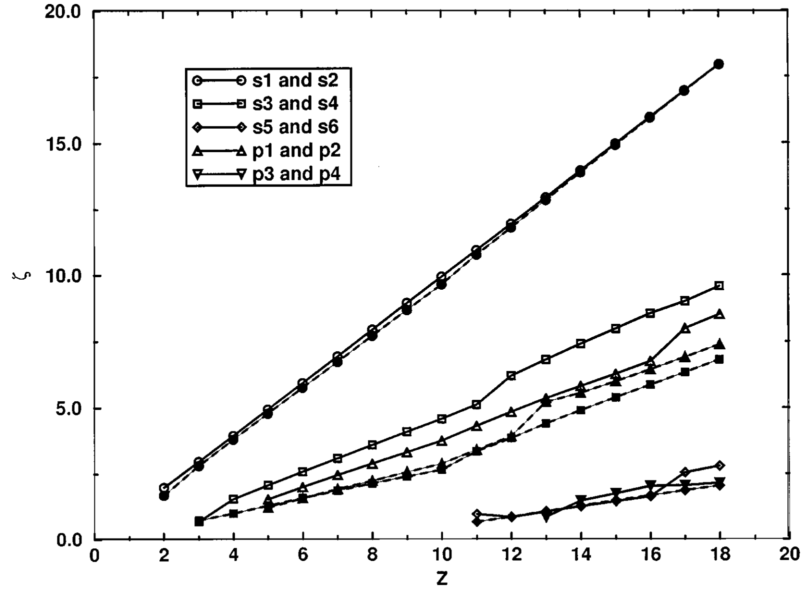


Fig. 2. Variation of the optimum *s* and *p* exponents, *ζ*, in CDZ- and IDZ-SESTF as a function of atomic number, *Z*. *Open symbols* and *full lines* correspond to IDZ-SESTF values and *filled symbols* and *dashed lines* to CDZ-SESTF values

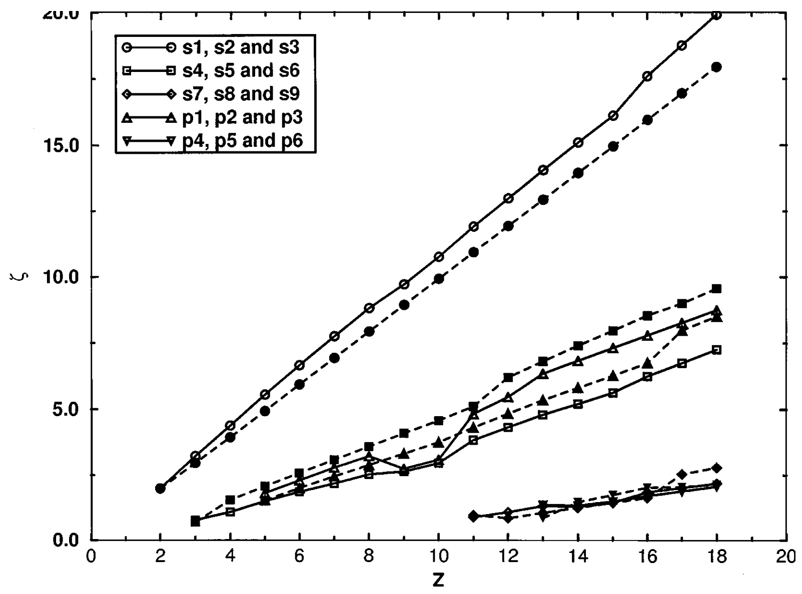


Fig. 3. Variation of the optimum *s* and *p* exponents, *ζ*, in CTZ- and ITZ-SESTF as a function of atomic number, *Z*. *Open symbols* and *full lines* correspond to ITZ-SESTF values and *filled symbols* and *dashed lines* to CTZ-SESTF value.

phenomenon was also observed [8] in NDZ-SESTF between $Z = 10$ and 11, but not in CDZ-SESTF as seen in Fig. 2. A difference in the optimum CDZ- and IDZ-SESTF exponents is also found for the $p1$ and $p2$ STFs; however, the exponents corresponding to the valence s and p orbitals exhibit similar values, more or less.

The optimum exponents for CTZ- and ITZ-SESTF also show approximate linearity against Z, as shown in Fig. 3. Except for a few cases, the observed linearity is slightly better in TZ SESTF than in DZ SESTF; however, the difference in the optimum exponents in CTZ- and ITZ-SESTF is larger for the innermost orbital than for the outer orbitals.

4 Summary

We developed DZ and TZ basis sets of STFs for the atoms from He to Ar, where the STF exponents corresponding to the same atomic subshells were restricted to be common for computational efficiency. However, the STF n were thoroughly optimized among integer values in order to reduce the energy loss by the use of common exponents. All these devices are directed towards molecular applications with existing computer codes [13]. Molecular tests of the present basis sets are planned in our laboratories.

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