Theor Chem Acc (2000) 104:146–152
DOI 10.1007/s002140000126

Theoretical
Chemistry Accounts

Regular article

Valence and correlated basis sets for the first-row transition atoms from Sc to Zn

Takeshi Noro[1], **Masahiro Sekiya**[1], **Toshikatsu Koga**[2], **Hisashi Matsuyama**[2]

[1] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
[2] Department of Applied Chemistry, Muroran Institute of Technology, Muroran 050-8585, Japan

Received: 8 October 1999 / Accepted: 17 January 2000

Abstract. Contracted Gaussian-type function sets are developed for the valence 4*s* and 3*d* orbitals and for correlated functions of the first-row transition atoms from Sc to Zn. A segmented contraction scheme is used for its compactness and computational efficiency. The contraction coefficients and exponents of the valence and correlated sets are determined by minimizing the differences from weighted averages of accurate atomic natural orbitals for the $4s^23d^{n-2}$ and $4s^13d^{n-1}$ atomic states. The new basis sets give a well-balanced description for these configurations at the Hartree–Fock level and yield more than 97% of the atomic correlation energies predicted by accurate natural orbitals of the same size. Molecular tests of the present basis functions are performed for the FeCO molecule at complete-active-space self-consistent-field and at single and double excitation configuration interaction levels. The present sets show an accuracy similar to that of the averaged atomic natural orbital sets in spite of 3–5 times shorter computation time in the generation of two-electron integrals.

Key words: Basis sets – Valence functions – Correlated functions – Contracted Gaussian-type functions – First-row transition atoms

1 Introduction

Most of the available Gaussian-type function (GTF) basis sets [1–12] for the first-row transition metal atoms were determined for the $4s^23d^{n-2}$ configuration, in which the lowest *LS* term appears, except for the Cr and Cu atoms. In metal compounds, however, the predominant electronic configuration of the metals sometimes corresponds to other configurations, such as $4s^13d^{n-1}$ and $3d^n$. For example, the ground state of the Fe dimer dissociates into $\mathrm{Fe}(4s^23d^6)+\mathrm{Fe}(4s^23d^6)$, which has a repulsive potential curve. The strong binding in the Fe dimer comes from a different configuration which has the asymptote $\mathrm{Fe}(4s^13d^7)$ + $\mathrm{Fe}(4s^13d^7)$. These two configurations interchange at an intermediate separation. Thus, the use of a basis set which is able to describe both atomic states is strongly required in the study of systems including transition atoms. Hay [2] reported an additional *d* function whose exponent was optimized to minimize the energy of the $3d^n$ state. His *d* function gave vastly improved excitation energies from the ground $4s^23d^{n-2}$ to $4s^13d^{n-1}$ and $3d^n$ configurations. Pou-Amérigo et al. [10] published contracted GTF (CGTF) basis sets using a general contraction scheme and the atomic natural orbital (ANO) approach, where they averaged density matrices over $3d^n$, $4s^13d^{n-1}$, and $4s^23d^{n-2}$ configurations for a neutral atom as well as the ground-state neutral atom in an external electric field and its ground-state cation. The results showed well-balanced features in molecular applications.

Recently [13, 14], we proposed a new method for the construction of compact, yet efficient, polarization function sets. Our method uses CGTFs in a segmented form for polarization functions, where the contraction coefficients and exponents of GTFs are so determined as to minimize the difference between the functions and the accurate natural orbitals (NOs) in polarization space. The method has been successfully applied to the atoms from He to Ar, except for Li and Na. The new polarization functions have been shown to reproduce more than 98% of the atomic correlation energies predicted by accurate NOs of the same size.

In the present article we apply the proposed method to the development of new basis sets for 4*s* and 3*d* valence orbitals and *s* and *d* correlated functions as well as *p*, *f*, and *g* polarization functions of the first-row transition metals from Sc to Zn. Hereafter, all the additional basis functions including polarization functions will be referred to as correlated functions. Since our aim is to construct new CGTF sets which are smaller than, but have a quality similar to, the ANO sets, we consider two atomic configurations $4s^23d^{n-2}$ and

---

Correspondence to: T. Noro

$4s^1 3d^{n-1}$ for all the neutral transition atoms in the determination of segmented CGTF basis sets except for Zn, where we employ a single configuration $4s^2 3d^{10}$. The next section outlines our computational procedures and presents the results for atomic valence and correlated functions. In Sect. 3, molecular tests of the present basis sets are given for the FeCO molecule in comparison with the ANO sets.

2 Atomic valence and correlated functions

2.1 Computational method

To obtain accurate reference NOs for the generation of valence and correlated CGTF sets, we first performed single and double substitution configuration interaction (SDCI) calculations on the lowest terms of two configurations $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ for the atoms from Sc to Cu, by using the ATOMCI program [15]. For the Zn atom, we did an SDCI calculation only for the ground state $4s^2 3d^{10}$ (^{1}S). We only considered correlation effects among the 4*s* and 3*d* electrons, and the inner 1*s*–3*s*, 2*p*, and 3*p* orbitals were treated as a frozen core. In these calculations, primitive GTF sets of (26*s*20*p*15*d*) for Sc to Ni and (26*s*20*p*16*d*) for Cu and Zn were employed. These sets were generated by enlarging the well-tempered basis sets [6, 8] of (26*s*17*p*13*d*) for Sc to Ni and of (26*s*17*p*14*d*) for Cu and Zn by using the same tempering parameters of the original set. For the *f* and *g* functions, we employed the same size and exponents as the *d* functions; 15*f*15*g* for Sc to Ni and 16*f*16*g* for Cu and Zn. Hereafter, we simply call these extended sets well-tempered sets. The NOs were then obtained by diagonalizing the density matrices. Judging from the size of basis functions, we consider the present NOs are sufficiently close to the exact NOs and, hence, we hereafter refer to them as accurate NOs. Because of the frozen-core approximation applied, the inner 1*s*–3*s*, 2*p*, and 3*p* NOs are equivalent to the Hartree–Fock (HF) orbitals. Thus, these five orbitals are simply referred to as HF orbitals.

Following our previous idea [13, 14], both the contraction coefficients and exponents of the valence 4*s* and 3*d* CGTFs were determined by minimizing the difference between the CGTFs and accurate valence NOs. Since this optimization can be performed independently for each symmetry specified by the azimuthal quantum number, *l*, we define for a respective symmetry a functional

$$\Delta = \sum_{k=1}^{N} n_k \int \mathrm{d}r \, |\lambda_k(\vec{r}) - \psi_k(\vec{r})|^2 w(\vec{r}) \ , \tag{1}$$

$$\psi_k(r) = \sum_{i=1}^{M} C_{ki} \, \chi_i(\vec{r}) \ , \tag{2}$$

where $\{\lambda_k\}$ are 4*s* or 3*d* NOs of the lowest terms of both the $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ configurations, $\{n_k\}$ are the occupation numbers, N (2 for Sc-Cu, 1 for Zn) is the number of NOs, M is the size of a CGTF basis set, $\{\chi_i\}$, and $w(\vec{r})$ is a weight function. In the construction of the 4*s* valence CGTFs, the 1*s*–3*s* HF orbitals of the ground state were added to $\{\chi_i\}$ to represent the contribution from the core functions whose CGTF approximations were not considered in this work. Namely, the present valence sets were determined under the condition that the accurate core orbitals already exist. In the functional (Eq. 1), the $\{n_k\}$, originally introduced [13, 14] to incorporate the relative significance of NOs in correlated space, were set equal to unity in the construction of valence sets to assign the same weight to the two configurations. We employed $1/r^2$ as the weight function since in previous work [13] it was found to give the most appropriate results. The conjugated direction algorithm [16] was used for nonlinear optimization of the GTF exponents and contraction coefficients, which minimize the functional Δ defined by Eq. (1).

Essentially the same procedure was used to determine the correlated CGTF sets for the s, p, d, f, and g symmetries, except that the $\{n_k\}$ were kept as they were. The contraction coefficients and exponents of CGTFs for a symmetry were so determined as to minimize the difference from the n_k-weighted average of the accurate NOs of the two configurations $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ in that symmetry; therefore, the number of NOs referred to is just twice the number of correlated CGTFs determined in each symmetry, except for Zn. In order to take into account the contribution from the core, the fixed HF orbitals from the ground state, 1*s*–3*s* for the *s* symmetry and 2*p* and 3*p* for the *p* symmetry, were added to $\{\chi_i\}$. For the *s* and *d* symmetries, the 4*s* and 3*d* NOs from the both configurations were also included. As was the case of the present valence sets, the correlated CGTF sets were constructed under the assumption that accurate orbitals are known for occupied space.

2.2 Valence functions

For the valence 4*s* and 3*d* orbitals, we needed at least double-zeta functions to obtain a good description of the different valence orbitals of the two configurations simultaneously. A double-zeta basis set was also constructed for the Zn atom, though only the $4s^2 3d^{10}$ configuration was considered.

In order to determine appropriate contraction sizes of valence functions, we carried out test calculations for the $4s^2 3d^6$ (^{5}D) and $4s^1 3d^7$ (^{5}F) states of the Fe atom. We tested several types of contractions for *s* and *d* functions. The total energies from two CGTFs for the $4s^2 3d^6$ (^{5}D) and $4s^1 3d^7$ (^{5}F) states are listed in Table 1 and are compared with those from the well-tempered set, where the single-digit figures in the parentheses stand for the numbers of primitive GTFs. In our test calculations for *s* functions, we used HF orbitals generated by the well-tempered set for the 1*s*–3*s*, 2*p*, 3*p*, and 3*d* orbitals. The smallest (11) set has a difference of 1–4 mhartrees in the total energies from the well-tempered set. The difference reduces to 0.1–0.4 mhartrees with (31) contraction. We therefore employed this (31) contraction for the *s* function. In pilot calculations for *d* functions, we used well-tempered HF orbitals for the 1*s*–4*s*, 2*p*, and 3*p* functions. A larger set was required for *d* functions to obtain a quality similar to the *s* set. Even when we used a *d* (62) set, the total energy differences from the well-tempered values were still 10 times larger than for the *s* (31) set; however, the discrepancy in the energy separation, ^{5}F – ^{5}D, is smaller than that of the *s* set. Thus, we picked up the (62) contraction for the *d* set. This set yields 0.066351 hartrees for the separation energy, which is only 0.3 mhartrees different from that of the well-tempered set.

The calculated HF energies of the $4s^23d^{n-2}$ and $4s^13d^{n-1}$ configurations are summarized for the first-row transition atoms in Table 2. In these calculations, we used the present (31) and (62) sets for 4*s* and 3*d* orbitals and the rest of the occupied orbitals were fixed at the HF orbitals obtained from the well-tempered set. The differences in the HF total energies obtained by the present and well-tempered sets range from 0.5 to 6 mhartrees; however, the discrepancies in the energy separation between the $4s^23d^{n-2}$ and $4s^13d^{n-1}$ states are only 0.4–0.8 mhartrees. We conclude that the present valence sets are well balanced at the HF level.

Table 1. Comparison of the Hartree–Fock (HF) total and excitation energies (hartrees) of various valence contracted Gaussian-type function (CGTF) sets for the $4s^23d^6$ (^{5}D) and $4s^13d^7$ (^{5}F) states of the Fe atom

	^{5}D	^{5}F	^{5}F–^{5}D
Valence *s* sets[a]			
(11)	−1262.439937	−1262.376206	0.063732
(21)	−1262.443256	−1262.377079	0.066177
(31)	−1262.443518	−1262.377215	0.066303
(32)	−1262.443526	−1262.377228	0.066298
(41)	−1262.443525	−1262.377225	0.066300
Valence *d* sets[b]			
(51)	−1262.432306	−1262.362006	0.070300
(52)	−1262.433955	−1262.369737	0.064218
(61)	−1262.440599	−1262.370259	0.070340
(62)	−1262.440548	−1262.374455	0.066093
(63)	−1262.440466	−1262.374300	0.066166
s(31)*d*(62)[c]	−1262.440436	−1262.374085	0.066351
Well-tempered set	−1262.443633	−1262.377582	0.066050

[a] The HF orbitals from the well-tempered set were used for 1*s*–3*s*, 2*p*, 3*p*, and 3*d*

[b] The HF orbitals from the well-tempered set were used for 1*s*–4*s*, 2*p*, and 3*p*

[c] The HF orbitals from the well-tempered set were used for 1*s*–3*s*, 2*p*, and 3*p*

2.3 Correlated functions

For the correlated sets of the atoms from He to Ar, we previously [13, 14] employed two GTFs in a segmented contraction form for the first function of each symmetry, while the other functions were kept as primitive GTFs. For the transition atoms from Sc to Zn, we also need two GTFs for the first function of each of the *p*, *d*, and *g* correlated sets. For the first *f* function, however, three GTFs are needed to attain a quality similar to the correlated functions of the other symmetry.

We constructed correlated function sets (2*p*)/[1*p*], (1*s*2*p*2*d*)/[1*s*2*p*1*d*], (2*s*3*p*3*d*3*f*)/[2*s*3*p*2*d*1*f*], and (3*s*4*p*3*d*4*f*2*g*)/[3*s*4*p*3*d*2*f*1*g*] for the atoms from Sc to Zn. In order to examine the quality of the present correlated functions, we carried out test SDCI calculations on the lowest terms of the $4s^23d^{n-2}$ and $4s^13d^{n-1}$ configurations of each atom, except for the Zn atom, where we calculated only the $4s^23d^{10}$ (^1S) state. As the inner 1*s*–3s, 2*p*, and 3*p* parts, the respective HF orbitals were used for each state. For the valence 4*s* and 3*d* orbitals, we used the HF orbitals of both states simultaneously, because the present correlated basis sets were determined under the condition that the 4*s* and 3*d* orbitals of these two states exist.

The calculated correlation energies are summarized in Table 3. In all cases, the present basis sets reproduce more than 97% of the atomic correlation energies obtained by the accurate NOs of the same size. For the $4s^13d^2$ (^{4}F) state of Sc, the present 1*p* set gave exactly the same correlation energy as the accurate NOs, since the whole correlation energy comes from the excitation among two sets of 4*s* and 3*d* HF orbitals and a single *p* correlated function does not contribute to this state. For the excited states of V, Mn, and Co atoms, the present set yields more than 100% of the correlation energies of the accurate NOs. The present correlated basis sets were obtained under the condition that the valence orbitals of the two configurations exist, whereas the NOs were determined only for each atomic state with no extra valence orbitals from the counterpart configuration. Since our test calculations were performed under the same condition, the calculated correlation energy exceeds 100% of that of the accurate NOs for the three cases.

Finally, we tested the total quality of the present valence and correlated sets. The calculated SDCI energies and excitation energies of the Fe atom are shown as an example in Table 4. The discrepancies of the SDCI

Table 2. The HF total energies (hartrees) of the ground and excited states for the first row transition atoms. The HF orbitals from the well-tempered set were used for 1*s*–3*s*, 2*p*, and 3*p*. The symbol δ means the errors relative to near HF-limit values

Atom	State	Energy	δ	State	Energy	δ
Sc	$4s^23d^1$ (^{2}D)	−759.735211	0.000490	$4s^13d^2$ (^{4}F)	−759.697794	0.000976
Ti	$4s^23d^2$ (^{3}F)	−848.405131	0.000848	$4s^13d^3$ (^{5}F)	−848.384570	0.001567
V	$4s^23d^3$ (^{4}F)	−942.882951	0.001367	$4s^13d^4$ (^{6}D)	−942.877559	0.002204
Cr	$4s^13d^5$ (^{7}S)	−1043.354423	0.001920	$4s^23d^4$ (^{5}D)	−1043.307963	0.001822
Mn	$4s^23d^5$ (^{6}S)	−1149.863643	0.002582	$4s^13d^6$ (^{6}D)	−1149.740986	0.002944
Fe	$4s^23d^6$ (^{5}D)	−1262.440432	0.003201	$4s^13d^7$ (^{5}F)	−1262.374058	0.003524
Co	$4s^23d^7$ (^{4}F)	−1381.410697	0.003818	$4s^13d^8$ (^{4}F)	−1381.354028	0.004314
Ni	$4s^23d^8$ (^{3}F)	−1506.866331	0.004531	$4s^13d^9$ (^{3}D)	−1506.818824	0.005154
Cu	$4s^13d^{10}$ (^{2}S)	−1638.957628	0.006067	$4s^23d^9$ (^{2}D)	−1638.944769	0.005265
Zn	$4s^23d^{10}$ (^{1}S)	−1777.844501	0.003571			

Table 3. Correlation energies (hartrees) and excitation energies (eV) for the first-row transition atoms

Correlated functions	Correlation energy (%[a])		Excitation energy (Accurate)[b]
	Ground state	Excited state	
Sc			
$+1p$	0.034781 (99.74)	0.009650 (100.00)	1.689 (1.691)
$+1s2p1d$	0.035864 (99.14)	0.011140 (99.27)	1.678 (1.684)
$+2s3p2d1f$	0.040219 (99.44)	0.018566 (99.63)	1.594 (1.598)
$+3s4p3d2f1g$	0.041188 (99.83)	0.020063 (98.85)	1.580 (1.575)
Ti			
$+1p$	0.038118 (99.69)	0.019325 (98.70)	1.051 (1.048)
$+1s2p1d$	0.042079 (99.07)	0.024328 (99.05)	1.023 (1.027)
$+2s3p2d1f$	0.051226 (99.47)	0.037440 (99.87)	0.915 (0.921)
$+3s4p3d2f1g$	0.054072 (99.69)	0.041121 (98.88)	0.892 (0.884)
V			
$+1p$	0.043657 (99.52)	0.030508 (97.95)	0.482 (0.470)
$+1s2p1d$	0.052890 (98.83)	0.041094 (98.98)	0.445 (0.451)
$+2s3p2d1f$	0.069171 (99.49)	0.063317 (100.33)	0.283 (0.299)
$+3s4p3d2f1g$	0.074936 (99.65)	0.070058 (99.00)	0.257 (0.245)
Cr			
$+1p$	0.040186 (97.82)	0.050751 (99.21)	0.979 (0.993)
$+1s2p1d$	0.057595 (99.08)	0.067316 (98.79)	1.002 (0.995)
$+2s3p2d1f$	0.091351 (99.61)	0.094239 (99.48)	1.188 (1.185)
$+3s4p3d2f1g$	0.100658 (99.02)	0.103733 (99.67)	1.183 (1.201)
Mn			
$+1p$	0.053992 (98.70)	0.100032 (99.48)	2.909 (2.906)
$+1s2p1d$	0.081267 (98.65)	0.069395 (98.83)	2.817 (2.833)
$+2s3p2d1f$	0.120321 (98.97)	0.147850 (100.61)	2.579 (2.637)
$+3s4p3d2f1g$	0.133663 (99.64)	0.164921 (99.23)	2.477 (2.456)
Fe			
$+1p$	0.072065 (98.42)	0.087654 (98.84)	1.373 (1.377)
$+1s2p1d$	0.114917 (98.90)	0.196810 (99.74)	1.330 (1.332)
$+2s3p2d1f$	0.171064 (99.10)	0.132153 (99.10)	1.097 (1.125)
$+3s4p3d2f1g$	0.193193 (99.49)	0.221192 (99.40)	1.035 (1.026)
Co			
$+1p$	0.082106 (98.02)	0.107568 (100.41)	0.836 (0.893)
$+1s2p1d$	0.143074 (98.85)	0.168350 (99.02)	0.841 (0.840)
$+2s3p2d1f$	0.217966 (99.14)	0.252624 (98.57)	0.585 (0.537)
$+3s4p3d2f1g$	0.247873 (99.43)	0.284613 (98.98)	0.529 (0.487)
Ni			
$+1p$	0.093896 (97.73)	0.128585 (98.72)	0.332 (0.346)
$+1s2p1d$	0.175033 (98.89)	0.207647 (99.34)	0.388 (0.404)
$+2s3p2d1f$	0.271941 (99.15)	0.314821 (99.66)	0.109 (0.143)
$+3s4p3d2f1g$	0.309942 (99.39)	0.355187 (99.22)	0.045 (0.020)
Cu			
$+1p$	0.146616 (98.64)	0.107971 (97.52)	1.423 (1.404)
$+1s2p1d$	0.245121 (99.40)	0.210502 (98.94)	1.314 (1.292)
$+2s3p2d1f$	0.377619 (99.63)	0.332813 (99.14)	1.591 (1.551)
$+3s4p3d2f1g$	0.424430 (99.24)	0.379778 (99.36)	1.587 (1.609)
Zn			
$+1p$	0.036042 (99.63)		
$+1s2p1d$	0.225827 (97.31)		
$+2s3p2d1f$	0.388972 (98.72)		
$+3s4p3d2f1g$	0.446450 (99.17)		

[a] The percentage shows the accuracy of the calculated correlation energy relative to the value of the accurate natural orbitals of the same size

[b] The excitation energies obtained from the accurate natural orbitals of the same size

energies from the corresponding accurate values are 0.003–0.006 hartrees for both states. The deviations in the excitation energies are less than 0.04 eV for all sets. We obtained similar results for the rest of the transition metals. Thus, we conclude that the present valence and correlated sets have well-balanced quality for both the $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ atomic configurations.

The exponents and contraction coefficients for the Fe atom are exemplified in Table 5. All the present basis sets for the atoms from Sc to Zn are available on the internet at http://setani.sci.hokudai.ac.jp/qc/basis/.

3 Molecular applications

For the FeCO molecule, there was a long discussion on which of the $^3\Sigma^-$ or $^5\Sigma^-$ states is more stable. Using the method of configuration interaction by perturbation

Table 4. The single and double substitution configuration interaction energies (hartrees) and excitation energies (eV) of the Fe atom from the present valence and correlated functions. The HF orbitals from the well-tempered set for each state were used for the 1*s*–3*s*, 2*p*, and 3*p* orbitals. The symbol δ means the errors relative to the values obtained by the accurate NOs of the same size

Correlated functions	^{5}D		^{5}F		Excitation energy (Accurate)[a]
	Energy	δ	Energy	δ	
+ 1*p*	−1262.512217	0.004636	−1262.460638	0.005624	1.404 (1.377)
+ 1*s*2*p*1*d*	−1262.554972	0.004905	−1262.504963	0.005969	1.361 (1.332)
+ 2*s*3*p*2*d*1*f*	−1262.611868	0.004389	−1262.571337	0.003577	1.103 (1.125)
+ 3*s*4*p*3*d*2*f*1*g*	−1262.634959	0.002857	−1262.596974	0.003145	1.034 (1.026)

[a] The excitation energies obtained from the accurate natural orbitals of the same size

Table 5. The valence and correlated CGTF sets for the Fe atom. For each polarization set, the first line gives the exponents and the second line gives the contraction coefficients

Valence functions						
s_1	2.167446	0.804508	0.110551			
	−0.043597	−0.247958	1.111733			
s_2	0.038975					
	1.000000					
d_1	153.149929	39.218533	13.124122	4.942013	1.918251	0.726308
	0.002484	0.024815	0.112497	0.294331	0.436439	0.400155
d_2	0.276957	0.102424				
	0.803321	0.267279				
Correlated functions						
+ 1*p*						
p	0.264887	0.093034				
	0.510199	0.567671				
+ 1*s*2*p*1*d*						
s	0.361252					
	1.000000					
p	0.465866			/0.131871		
	1.000000			/1.000000		
d	1.326670	0.441476				
	0.396523	0.709384				
+ 2*s*3*p*2*d*1*f*						
s	2.512824			/0.368494		
	1.000000			/1.000000		
p	0.812039			/0.326530	/0.105728	
	1.000000			/1.000000	/1.000000	
d	2.128789	1.011773		/0.412398		
	0.243499	0.796579		/1.000000		
f	6.519588	1.770151	0.484550			
	0.144177	0.556611	0.575686			
+ 3*s*4*p*3*d*2*f*1*g*						
s	3.090377			/0.551808	/0.097446	
	1.000000			/1.000000	/1.000000	
p	1.372477			/0.723424	/0.250136	/0.092407
	1.000000			/1.000000	/1.000000	/1.000000
d	1.960011			/0.807883	/0.315164	
	1.000000			/1.000000	/1.000000	
f	14.290381	4.403054	1.616008	/0.557672		
	0.054218	0.371259	0.721524	/1.000000		
g	3.109895	0.847751				
	0.428616	0.770539				

with multiconfigurational zeroth-order wave functions selected by an iterative process, Berthier and coworkers [17] reported $^{3}\Sigma^{-}$ as the ground state, while Barnes et al. [18] found that $^{5}\Sigma^{-}$ is lower using modified coupled-pair functional techniques. More recently, Adamo and Lelj [19] reported the $^{3}\Sigma^{-}$ state is 5.5 kcal/mol more stable than the $^{5}\Sigma^{-}$ state by a density functional theory method. Villalta and Leopold [20] have investigated the photoelectron spectrum of the FeCO^{-} ion. They have assigned the $^{3}\Sigma^{-}$ state as the ground state of FeCO and the $^{5}\Sigma^{-}$ state as the excited state lying 1135 cm^{-1} (3.6 kcal/mol) higher in energy.

In order to examine the quality of the present 4*s* and 3*d* valence and correlated functions, we performed test calculations on the ground $^{3}\Sigma^{-}$ state and the first excited

Table 6. Total energies and equilibrium internuclear distances of the FeCO molecule calculated using the complete-active-space self-consistent-field approach

	Basis set	R (Fe—C) (Å)	R(C—O) (Å)	Total energy (hartrees)	Excitation energy (kcal/mol)
$^3\Sigma^-$ state					
Present	Small	1.790	1.151	−1375.19335	
	Medium-sized	1.795	1.147	−1375.20142	
	Large	1.797	1.147	−1375.20320	
ANO	Small	1.787	1.153	−1375.24120	
	Medium-sized	1.796	1.150	−1375.24877	
	Large	1.796	1.150	−1375.24963	
Experimental [24]		1.727	1.159		
$^5\Sigma^-$ state					
Present	Small	1.879	1.154	−1375.20070	−4.61
	Medium-sized	1.879	1.150	−1375.21000	−5.39
	Large	1.879	1.150	−1375.21233	−5.73
ANO	Small	1.873	1.156	−1375.25046	−5.81
	Medium-sized	1.876	1.153	−1375.25825	−5.95
	Large	1.876	1.153	−1375.25935	−6.10

$^5\Sigma^-$ state of the FeCO molecule by using the ALCHEMY II program package [21]. For the Fe atom, minimal basis functions corresponding to the $1s$–$3s$, $2p$, and $3p$ orbitals were taken from the (743/74) set of Koga et al. [11], while the $4s$ and $3d$ valence functions were from this work. We examined three different sizes of correlated functions denoted as small, medium-sized, and large sets. The small set consisted of a $1s2p1d$ set augmented with an f correlated function which was generated by the procedure described in Sect. 2 with two f primitive GTFs[1]. We used $2s3p2d1f$ and $3s4p3d2f1g$ given in Table 5 for the medium-sized and large sets, respectively. For the carbon and oxygen atoms, the valence s and p functions were taken from Tatewaki and Koga [22], whose $2s$ and $2p$ functions were split into triple-zeta functions. The polarization functions, $1d$ for the small set and $2d1f$ for the medium-sized and large sets, were taken from our previous study [13]. For comparison, the ANO sets with precisely the same sizes were also examined.

The geometries R(Fe—C) and R(C—O) were optimized using the complete-active-space self-consistent-field (CASSCF) approach, assuming a linear structure. The active space in the CASSCF calculations consisted of 10-13a_1, 3-5b_1, 3-5b_2, and 1a_2 orbitals in C_{2v} symmetry, where 14 electrons in the $3d$ and $4s$ orbitals of the Fe atom and in the $2p$ orbitals of the C and O atoms were considered as active. The total energies and the equilibrium geometries for the $^3\Sigma^-$ and $^5\Sigma^-$ states of the FeCO molecule are compared in Table 6. The present sets give total energies higher than the ANO set by 0.04–0.05 hartrees, since the ANO set included much larger functions to describe the core orbitals; however, both sets predict essentially the same equilibrium geometry and excitation energy. The CASSCF calculations show that the $^3\Sigma^-$ state is not the lowest state but lies about 6 kcal/mol above the $^5\Sigma^-$ state.

We next performed multireference single and double excitation configuration interaction (MRSDCI) calculations with the small and medium-sized basis sets. For the $^5\Sigma^-$ state, we chose reference configurations from those with coefficients larger than 0.1 in the CASSCF wave functions. For the $^3\Sigma^-$ state, on the other hand, we employed a smaller threshold of 0.07 instead of 0.1 so that the weights of reference space in the resultant MRSDCI wave functions of $^3\Sigma^-$ and $^5\Sigma^-$ become almost the same. In these calculations, we took correlation effects of 18 valence electrons into account. Total energies for the ground and first excited states of the FeCO molecule at the equilibrium geometry obtained by the CASSCF calculations are shown in Table 7. The excitation energies are also summarized in Table 7. Although we included the valence electron correlation, the $^3\Sigma^-$ state is still higher than the $^5\Sigma^-$ state by 3.6–4.5 kcal/mol. Inclusion of the Davidson correction [23] lowers the $^3\Sigma^-$ state, which is now 0.4 or 1.1 kcal/mol more stable than the $^5\Sigma^-$ state.

The computation times of the two-electron integrals in the CASSCF/MRSDCI calculations are compared in Table 8. The present set is 3–5 times faster than the ANO set. Thus, the present basis sets are much more efficient than the ANO sets in the post-HF calculations, especially in the determination of the potential-energy surfaces.

4 Summary

We developed $4s$ and $3d$ valence CGTF sets and $(2p)/[1p]$, $(1s2p2d)/[1s2p1d]$, $(2s3p3d3f)/[2s3p2d1f]$, and $(3s4p3d4f2g)/[3s4p3d2f1g]$ correlated CGTF sets for the first-row transition metal atoms from Sc to Zn in segmented contraction forms. In the determination of the contraction coefficients and exponents, we minimized

---

[1] We also constructed a smaller f contracted function with two primitive GTFs. Its performance is slightly worse than the f function with three primitive GTFs shown in Table 5. The whole sets including these smaller sets are available on the internet at http://setani.sci.hokudai.ac.jp/qc/basis/

Table 7. The total and excitation energies of the FeCo molecule. The values in parentheses were obtained by using the multireference analogue of Davidson correction

Basis set	Total energy (hartrees)		Excitation energy (kcal/mol)
	$^3\Sigma^-$	$^5\Sigma^-$	
Present			
Small	−1375.59987 (−1375.66317)	−1375.60557 (−1375.66149)	−3.58 (1.05)
Medium-sized	−1375.65453 (−1375.72366)	−1375.66174 (−1375.72299)	−4.52 (0.42)
ANO			
Small	−1375.64707 (−1375.71179)	−1375.65417 (−1375.71105)	−4.46 (0.46)
Medium-sized	−1375.69690 (−1375.76674)	−1375.70531 (−1375.76696)	−5.28 (−0.14)
Experimental [20]			3.6

Table 8. Comparison of the computation times for the generation of two-electron integrals on an IBM RS/6000 (model 3CT) workstation

Basis set	Present (s)	ANO (s)
Small	183	845
Medium-sized	549	1591
Large	992	3416

the differences between the CGTFs and the accurate atomic NOs of both the $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ atomic configurations.

The present valence 4*s* and 3*d* functions show well-balanced features in HF calculations of the $4s^2 3d^{n-2}$ and $4s^1 3d^{n-1}$ atomic states. Despite their smallness, all the present correlated sets reproduce more than 97% of the atomic correlation energies predicted by the accurate atomic NOs. Test calculations on the FeCO molecule were performed for the ground $^3\Sigma^-$ and first excited $^5\Sigma^-$ states. At the CASSCF and MRSDCI levels, the present sets were confirmed to have accuracies similar to those of the averaged ANO sets with 3–4 times shorter computational time.

Finally, we note the portability of the present sets. In this work, we did not determine the basis set for inner orbitals, such as 1*s*–3*s*, 2*p*, and 3*p*; however, our test calculations indicated that the present sets can be combined with available basis sets for inner orbitals, which have a sufficient quality for atomic HF orbitals, to give satisfactory results in both CASSCF and configurations interaction calculations.

Acknowledgements. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

References

1. Wachters AJH (1970) J Chem Phys 52: 1033
2. Hay PJ (1977) J Chem Phys 66: 4377
3. (a) Tatewaki H, Huzinaga S (1979) J Chem Phys 71: 4339; (b) Tatewaki H, Huzinaga S (1980) J Comput Chem 1: 205
4. Huzinaga S, Andzelm J, Klobukowski M, Radio-Andzelm E, Sakai Y, Tatewaki H (1984) In: Huzinaga S (ed) Gaussian basis sets for molecular calculations. Elsevier, Amsterdam
5. Partridge H (1989) J Chem Phys 90: 1043
6. Huzinaga S, Miguel B (1990) Chem Phys Lett 175: 289
7. Schäfer A, Horn H, Ahlrichs R (1992) J Chem Phys 97: 2571
8. Huzinaga S, Klobukowski M (1993) Chem Phys Lett 212: 260
9. Bauschlicher CW Jr (1995) Theor Chem Acta 92: 183
10. Pou-Amérigo R, Merchán M, Nebot-Gil I, Widmark P-O, Roos BO (1995) Theor Chim Acta 92: 149
11. Koga T, Tatewaki H, Matsuyama H, Satoh Y (1999) Theor Chem Acc 102: 105
12. Rassolov VA, Pople JA, Ratner MA, Windus TL (1998) J Chem Phys 109: 1223
13. Noro T, Sekiya M, Koga T (1997) Theor Chem Acc 98: 25
14. Sekiya M, Noro T, Koga T, Matsuyama H (1998) J Mol Struct (THEOCHEM) 451: 51
15. (a) Sasaki F (1974) Int J Quantum Chem 8: 605; (b) Sasaki F, Sekiya M, Noro T, Ohtuski K, Osanai Y (1993) In: Clementi E (ed) Methods and techniques in computational chemistry: METECC-94, vol A. STEF, Cagliari, pp 163–219
16. Powell MJD (1964) Comput J 7: 155
17. (a) Berthier G, Daoudi A, Suard M (1988) J Mol Struct (THEOCHEM) 179: 407; (b) Barbier C, Berthier G, Daoudi A, Suard M (1988) Theor Chim Acta 73: 419
18. Barnes LA, Rosi M, Bauschlicher CW Jr (1991) J Chem Phys 94: 2031
19. Adamo C, Lelj F (1995) J Chem Phys 103: 10605
20. Villalta PW, Leopold DG (1993) J Chem Phys 98: 7730
21. (a) Lengsfield BH III (1980) J Chem Phys 73: 382; (b) Liu B, Yoshimine M (1981) J Chem Phys 74: 612; (c) Lengsfield BH III, Liu B (1981) J Chem Phys 75: 478
22. Tatewaki H, Koga T (1996) J Chem Phys 104: 8493
23. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8: 278
24. Tanaka K, Shirasaka M, Tanaka T (1997) J Chem Phys 106: 6820