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Valence 4*p* functions for the first-row transition metal atoms

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Abstract. For the valence 4*p* orbitals of the first-row transition metal atoms Sc through Zn, Gaussian-type basis functions are developed referring to excited $3d^m4s^14p^1$ electronic configurations. Molecular tests of the present work 4*p* sets are performed for the Cu atom, the diatomic Cu_2 molecule, and Cu_9 and Cu_{13} clusters, and the results are compared with those from two literature sets.

Key words: Valence 4*p* basis functions – Gaussian-type functions – First-row transition atoms

1 Introduction

Many Gaussian-type function (GTF) basis sets have been proposed for molecular calculations with [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] and without [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25] contractions. These basis sets were constructed mainly based on the atomic ground state, and hence they contained no appropriate basis functions for orbitals unoccupied in the ground state. However, we know that, for alkali, alkaline earth, and transition metal atoms, the valence *p* functions are very important; for example, they comprise the *sp* band with the valence *s* orbital in metals and large metallic clusters. Recently, we have developed [26] the valence *p* sets for alkali and alkaline earth atoms, referring to excited electronic configurations of these atoms. For the first transition metal atoms, two compact 4*p* basis sets have been reported in the literature by Wachters [12] and by Huzinaga and others [5]. Large 4*p* sets were also constructed [24, 25] using natural orbitals, but we concentrate on small basis sets to which we commit ourselves in this work. Wachters [12] generated the 4*p* sets for the transition metal atoms using $3d^m4p^2$ configurations except for Cu, where $3d^{10}4p^1$ was assumed. Huzinaga and colleagues [5] proposed 4*p* sets by maximizing their radial overlaps with 4*s* orbitals. In the present paper, we report new 4*p* sets for the first-row transition metal atoms using an excited $3d^m4s^14p^1$ electronic configuration. The present work *p* sets are compared with those of Wachters [12] and Huzinaga [5] in test calculations of the Cu atom, the diatomic Cu_2 molecule, and Cu_9 and Cu_{13} clusters.

2 Method of calculations and atomic results

Our purpose is to obtain 4*p* orbitals of a near Hartree-Fock quality with short contracted GTFs (CGTFs) in a way similar to the cases of the alkali and alkaline earth atoms [26] and to look into the possibility of using them as valence 4*p* sets. We used three *p*-type primitive GTFs to describe the 4*p* orbitals. The atomic configurations used to determine the 4*p* orbitals are $3d^m4s^14p^1$ for all the first-row transition metal atoms except for Cr and Cu, for which $3d^m4p^1$ is considered. Table 1 explicitly summarizes the electronic configurations and terms examined. The basis sets employed were (7433/743/7) for the former eight atoms and (743/743/7) for the latter two atoms, where the slashes distinguish the symmetries *s*, *p*, and *d* and the single digit figures indicate the numbers of primitive GTFs in each CGTF. The open-shell self-consistent field (SCF) method proposed by Roothaan and Bagus [27] was used for atomic Hartree-Fock calculations. The exponent parameters and the expansion coefficients of the respective CGTFs were treated as nonlinear parameters as before [8, 9, 10, 26] and Powell's method [28, 29] was employed for their optimizations.

The calculated total (E) and excitation (ΔE) energies are shown in Table 1 as well as the corresponding numerical Hartree-Fock (NHF) values. Although the total energy differences between the CGTF and NHF calculations are in the range of 0.02–0.05 hartrees, the excitation energy differences between the two calculations are one order smaller (<0.002 hartrees), indicating that the present work CGTF sets have a sufficient quality for describing the atomic 4*s* and 4*p* orbitals.

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Table 1. Comparison of the present work total energies E and excitation energies ΔE (in hartrees) with the NHF values[a]

Z	Atom	Configuration	State	Method	E(excited)	E(ground)	ΔE
21	Sc	[Ar]$3d^1 4s^1 4p^1$	^{4}F	NHF	−759.700623	−759.735720	0.035097
				CGTF	−759.680214	−759.714978	0.034764
22	Ti	[Ar]$3d^2 4s^1 4p^1$	^{5}G	NHF	−848.372273	−848.406000	0.033727
				CGTF	−848.349773	−848.383126	0.033353
23	V	[Ar]$3d^3 4s^1 4p^1$	^{6}G	NHF	−942.851304	−942.884340	0.033036
				CGTF	−942.826553	−942.859177	0.032624
24	Cr	[Ar]$3d^5 4p^1$	^{7}P	NHF	−1043.260288	−1043.356380	0.096092
				CGTF	−1043.232195	−1043.327991	0.095796
25	Mn	[Ar]$3d^5 4s^1 4p^1$	^{8}P	NHF	−1149.827058	−1149.866250	0.039192
				CGTF	−1149.797316	−1149.836033	0.038717
26	Fe	[Ar]$3d^6 4s^1 4p^1$	^{7}D	NHF	−1262.403618	−1262.443670	0.040052
				CGTF	−1262.371090	−1262.410591	0.039501
27	Co	[Ar]$3d^7 4s^1 4p^1$	^{6}F	NHF	−1381.356226	−1381.414550	0.058324
				CGTF	−1381.320725	−1381.378451	0.057726
28	Ni	[Ar]$3d^8 4s^1 4p^1$	^{5}G	NHF	−1506.797875	−1506.870910	0.073035
				CGTF	−1506.759222	−1506.831587	0.072365
29	Cu	[Ar]$3d^{10} 4p^1$	^{2}P	NHF	−1638.851432	−1638.963740	0.112308
				CGTF	−1638.807434	−1638.919153	0.111719
30	Zn	[Ar]$3d^{10} 4s^1 4p^1$	^{3}P	NHF	−1777.750100	−1777.848120	0.098020
				CGTF	−1777.705491	−1777.801778	0.096287

[a] In the excited state calculations, the (743/743/7) set is used for Cr and Cu, while the (7433/743/7) set is used for the other atoms. The ground-state CGTF total energies are from the (7433/74/7) set calculated by Koga and co-workers [10]

The optimum exponents e_i for the $4p$ orbitals are collected in Table 2 and compared with those of Wachters [12] and of Huzinaga and colleagues [5]. The expansion coefficients c_i of the present work $4p$ GTFs are listed in Table 3. From Table 2 we see that the exponents reported by Wachters [12] and Huzinaga [5] are close to each other, although the methods used are completely different. The distribution of the exponents obtained from the present work calculations covers those of Wachters and Huzinaga.

3 Atomic and molecular test calculations

The new sets were tested by using the Cu_n system. First, calculations on the Cu atom and the Cu_2 molecule were performed. The basis set is common to the two species: (74321/7211/4111) generated from the (7433/74/7) CGTF set reported in [10]. Although it is a minimal set, the total energy, −1638.9192 hartrees, calculated by (7433/74/7) is lower than that (−1638.7867 hartrees) of Wachters' (61111111/5112/32) set [12] and equal to that (−1638.9192 hartrees) of Schaefer and co-workers' (842111/631/411) set [7]. Two correlating *f*-type functions with exponents 0.683 and 0.375 and three (present work) or two (Huzinaga [5] and Wachters [12]) *p*-type polarization functions are further added in the atomic and diatomic calculations. The size of the present work set is $5s4p4d2f + [3p/3p] = (74321/7211 + 111/4111/11)$ and the sizes of Wachters' and Huzinaga's are $5s4p4d2f + [2p/2p] = (74321/7211 + 11/4111/11)$, where the symbols in the brackets before and after the slash indicate the numbers of CGTFs and primitive GTFs; in the atomic and diatomic calculations, uncontracted polarization functions are used.

For the Cu atom, the ground state $3d^{10}4s^1$ ^{2}S and three excited states $3d^{10}4p^1$ ^{2}P, $3d^9$ $4s^1 4p^1$ ^{4}P, and $3d^9 4s^1 4p^1$ ^{2}P are considered. The calculated total energies by the SCF and configuration interaction (CI) calculations with single and double excitations (SD) from the above reference configurations are shown in Table 4 together with the results obtained by Davidson correction (DC) [30]. The excitation energies are collected in Table 5. From Table 4 we see that, except for the SCF ground state where the present work total energy is only slightly ($2\text{–}3 \times 10^{-5}$ hartrees) higher than those of Huzinaga and Wachters, the new $4p$ set gives the lowest total energies irrespective of the methods and the states. The total energy differences between the present work and Huzinaga and the present work and Wachters are greater than 3×10^{-4} hartrees, showing better ability of the new set in describing the excited and correlating orbitals than the previous ones [5, 12]. From Table 5 we see that the excitation energies calculated by the present work set are always lowest, irrespective of the methods and states, as expected. In SCF, the energetic order of the calculated states is $3d^{10}4s^1$ ^{2}S < $3d^9 4s^1 4p^1$ ^{4}P < $3d^{10}4p^1$ ^{2}P < $3d^9 4s^1 4p^1$ ^{2}P, but the experimental result is $3d^{10}4s^1$ ^{2}S < $3d^{10}4p^1$ ^{2}P < $3d^9 4s^1 4p^1$ ^{4}P < $3d^9 4s^1 4p^1$ ^{2}P. The orders given by CI and CI + DC are the same as the experiment. The absolute value of the calculated correlation energies in the $3d^{10}$ shell is about 2 eV larger than that in $3d^9$, which reverses the energetic order predicted by SCF. The experimental excitation energy from $3d^{10}4s^1$ ^{2}S to $3d^{10}4p^1$ ^{2}P is 3.81 eV, while the CI (+DC) value is calculated to be 3.44 (3.50) eV, indicating that the correlation corrections between the $4s$ and core electrons and the relativistic effects for $3d^{10}4s^1$ ^{2}S are larger than those for $3d^{10}4p^1$ ^{2}P. More precise investigation is necessary to know the details of theses excited states, but it is beyond the scope of the present work.

For the Cu_2 molecule, the SCF and SDCI calculations were performed on the ground state, using the D_{2h}

Table 2. Comparison of the exponents for the $4p$ functions[a]

	Wachters	Huzinaga	Present work
	Sc		
e_1	0.089748	0.080	0.1046189
e_2	0.031032	0.026	0.0442003
e_3			0.0195215
	Cr		
e_1	0.120675	0.109	0.1328385
e_2	0.038610	0.036	0.0473598
e_3			0.0181215
	Co		
e_1	0.141308	0.141	0.2113104
e_2	0.043402	0.046	0.0811065
e_3			0.0314243
	Zn		
e_1	0.162455	0.176	0.2372305
e_2	0.047769	0.055	0.0876589
e_3			0.0328316
	Ti		
e_1	0.101561	0.090	0.1263502
e_2	0.034054	0.030	0.0527802
e_3			0.0226797
	Mn		
e_1	0.127650	0.119	0.1793631
e_2	0.040280	0.039	0.0708056
e_3			0.0282640
	Ni		
e_1	0.146588	0.153	0.2184648
e_2	0.044447	0.049	0.0827506
e_3			0.0316763
	V		
e_1	0.111248	0.099	0.1464669
e_2	0.036378	0.033	0.0601870
e_3			0.0251997
	Fe		
e_1	0.134915	0.130	0.2074709
e_2	0.041843	0.042	0.0807753
e_3			0.0317196
	Cu		
e_1	0.155065	0.142	0.1744028
e_2	0.046199	0.044	0.0560338
e_3			0.0201284

[a] See [12] for Wachters and [5] for Huzinaga

Table 3. Expansion coefficients of the present work $4p$ functions

	Sc	Ti	V	Cr	Mn
c_1	0.3945144	0.3469822	0.3168785	0.1978174	0.2757239
c_2	0.5353859	0.5462807	0.5516243	0.5504753	0.5556419
c_3	0.1586550	0.2022626	0.2325772	0.3724644	0.2796586
	Fe	Co	Ni	Cu	Zn
c_1	0.2654756	0.2577405	0.2514653	0.1625949	0.2412936
c_2	0.5567829	0.5555092	0.5543214	0.5337190	0.5523674
c_3	0.2917861	0.3039197	0.3141717	0.4355892	0.3312448

symmetry instead of $D_{\infty h}$. One ($\ldots 7\sigma_g^2$) and two ($\ldots 7\sigma_g^2 + \ldots 7\sigma_u^2$) reference functions were used in the CI calculations and are referred to as 1- and 2-reference CI, respectively. The 2-reference CI calculation gives the correct dissociation limit, while the 1-reference CI calculation does not. The total energies of the SCF, CI, and CI + DC of the 2-reference calculations are given in Table 6. The present work valence $4p$ GTFs always give the best total energies in the SCF and 1-reference CI calculations, but not for 2-reference CI and only for shorter bond distances in the CI + DC calculations. The calculated and experimental [32] spectroscopic constants are shown in Table 7. All the sets give almost the same results. We note that, in the case of 2-reference CI and CI + DC, the present work $4p$ set predicts a smaller dissociation energy D_e than the Huzinaga and Wachters sets. We recall that the present work valence $4p$ gives almost always the lowest total energy for the Cu atom, but not for the Cu_2 molecule in the 2-reference cases. This explains why the 2-reference CI and CI + DC give the smallest D_e with the present work $4p$. The 1-reference CI calculations in Table 7 give D_e of 0.53 eV, while Walch and co-workers [33] reported 1.2 eV. The present work D_e remains essentially unchanged (0.56 eV) even when 2 references are considered. We suspect that Walch and co-workers adopted the $(7\sigma_g)^1(7\sigma_u)^1\ {}^3\Sigma_u^+$ state at $R = 50$ bohrs as the dissociation limit to calculate D_e [34]. Inclusion of DC in 2-reference CI calculations considerably improves D_e (1.28–1.30 eV) compared to those obtained without DC.

We next discuss the first excited state designated as $7\sigma_g^1 7\sigma_u^1\ {}^1\Sigma_u^+$ [32]. The vertical excitation is observed with the excitation energy 2.70 eV. We performed SCF and 1-reference CI calculations for this state. The total energies of the ${}^1A_g$ and ${}^1B_{1u}$ states corresponding to $7\sigma_g^2\ {}^1\Sigma_g^+$ and $7\sigma_g^1 7\sigma_u^1\ {}^1\Sigma_u^+$ are shown in Table 8, where the notation of the 1- and 2-reference CIs applies to the ground state and the number of the reference for the excited $7\sigma_g^1 7\sigma_u^1\ {}^1\Sigma_u^+$ state is always fixed to one. The present work $4p$ set always gives the lowest total energies for the excited state irrespective of the method, showing the adequacy of the present work set to the excited state. The SCF and 2-reference CI excitation energies from the present work $4p$ are smaller than those from the other sets, which is in accord with what we have discussed above. The 1-reference CI gave essentially the same excitation energies for all the $4p$ sets, but the reason is not clear.

In the excited state, the SCF ${}^1\Sigma_u^+$ configuration is a dominant configuration even in CI; the weight for this configuration is always greater than 0.9. Examination of the gross atomic orbital population (GAOP) [35] shows that, in the ${}^1\Sigma_u^+$ state, GAOPs for the $4s$-like and $4p$ orbitals are 0.5 and 0.5 in this work, while those of Wachters and Huzinaga were 0.6 and 0.4. Moreover, GAOP for the most diffuse polarization function is 0.15, indicating its importance. Although the calculated excitation energies are close to each other, the characteristics of the $7\sigma_u$ orbitals are different. Before the calculations are performed we expected that $7\sigma_u$ would be more p-like but, as shown above, $7\sigma_u$ has a mixed character. In this context, we have failed to illustrate a typical example to show the effectiveness of the $4p$ set, but we can accept the importance of the very diffuse $4p$ through the present work calculations.

Table 4. Total energies E (in hartrees) for the ground and excited states of Cu

	Present work[a] (5s7p4d2f)	Huzinzga[b] (5s6p4d2f)	Wachters[b] (5s6p4d2f)
Ground state $3d^{10}4s^{1}\,{}^{2}S^{o}$			
SCF	−1638.920341	−1638.920368	−1638.920360
CI[c]	−1639.213729	−1639.213126	−1639.213398
CI + DC[d]	−1639.229755	−1639.228995	−1639.229341
Excited state $3d^{10}4p^{1}\,{}^{2}P^{o}$			
SCF	−1638.808246	−1638.805174	−1638.804568
CI[e]	−1639.087387	−1639.085400	−1639.085218
CI + DC[d]	−1639.101198	−1639.099406	−1639.099322
Excited state $3d^{9}4s^{1}4p^{1}\,{}^{4}P^{o}$			
SCF	−1638.827582	−1638.827120	−1638.827285
CI[f]	−1639.050707	−1639.049508	−1639.050041
CI + DC[d]	−1639.060041	−1639.058709	−1639.059310
Excited state $3d^{9}4s^{1}4p^{1}\,{}^{2}P^{o}$			
SCF[g]	−1638.801304	−1638.801042	−1638.801006
CI[h]	−1639.026065	−1639.025165	−1639.025474
CI + DC[d]	−1639.036830	−1639.035816	−1639.036198

[a] [74321/7211 + 111/4111/11] with f exponents 0.683 and 0.375
[b] [74321/7211 + 11/4111/11] with f exponents 0.683 and 0.375
[c] CI dimensions are 200, 166, and 166 for the present work, Huzinaga, and Wachters sets, respectively
[d] CI calculation with Davidson correction (see [30])
[e] CI dimensions are 327, 277, and 277 for the present work, Huzinaga, and Wachters sets, respectively
[f] CI dimensions are 1462, 1232, and 1232 for the present work, Huzinaga, and Wachters sets, respectively
[g] The result of two-dimensional $[3d^{9}4s^{1}(^{3}D)4p^{1} + 3d^{9}4s^{1}(^{1}D)4p^{1}]$ MCSCF calculations
[h] CI dimensions are 2518, 2117, and 2117 for the present work, Huzinaga, and Wachters sets, respectively

Table 5. Excitation energies ΔE (in eV) for the Cu atom

		Present work	Huzinaga	Wachters	Exptl.[a]
SCF					
$3d^{9}4s^{1}4p^{1}$	${}^{2}P^{o}$	3.239	3.247	3.248	5.686
$3d^{9}4s^{1}4p^{1}$	${}^{4}P^{o}$	2.524	2.537	2.533	4.923
$3d^{10}4p^{1}$	${}^{2}P^{o}$	3.050	3.135	3.151	3.806
$3d^{9}4s^{1}$	${}^{2}S^{o}$	0.0	0.0	0.0	0.0
CI[b]					
$3d^{9}4s^{1}4p^{1}$	${}^{2}P^{o}$	5.106	5.115	5.114	5.686
$3d^{9}4s^{1}4p^{1}$	${}^{4}P^{o}$	4.436	4.452	4.445	4.923
$3d^{10}4p^{1}$	${}^{2}P^{o}$	3.438	3.476	3.488	3.806
$3d^{9}4s^{1}$	${}^{2}S^{o}$	0.0	0.0	0.0	0.0
CI + DC[c]					
$3d^{9}4s^{1}4p^{1}$	${}^{2}P^{o}$	5.250	5.257	5.256	5.686
$3d^{9}4s^{1}4p^{1}$	${}^{4}P^{o}$	4.618	4.634	4.627	4.923
$3d^{10}4p^{1}$	${}^{2}P^{o}$	3.498	3.526	3.538	3.806
$3d^{9}4s^{1}$	${}^{2}S^{o}$	0.0	0.0	0.0	0.0

[a] See [31]
[b] See footnotes c, d, e, f, and h of Table 4
[c] See [30]

Test calculations are also performed on the square antiprism Cu_9 (Cu_4-Cu_5: C_{4v}) and cubooctahedron Cu_{13} (Cu_4-Cu_5-Cu_4: O_h) clusters. The bond distance between the nearest neighbors is assumed to be 4.83 bohrs, as observed in the solid. Below, we discuss only the results of the Cu_{13} cluster, since the conclusions deduced from the molecular calculations of the two clusters are very similar. The molecular symmetry used for Cu_{13} was D_{4h} instead of O_h. The parent molecular basis set, before valence 4p functions are incorporated, is (74321/74/61), generated from the same (7433/74/7) set used for Cu and Cu_2. Three contraction schemes for 4p GTFs are considered for cluster applications. They are [1p/3p], [2p/3p], and [3p/3p]. In the [2p/3p] sets, the two primitive GTFs with the largest exponents were contracted with the coefficients given in Table 3. Furthermore, we introduced a scaling factor of 2.4, which was so determined as to attain the minimum total energy of the diatomic Cu_2 molecule with a (74321/74/61) + [1p/3p] set at the internuclear distance 4.83 bohrs. The three exponents in any scaled 4p sets are generated by multiplying the scaling factor to those given in Table 2. We therefore prepared two 4p sets denoted as $[ip/3p]_{\mathrm{u}}$ and $[ip/3p]_{\mathrm{s}}$ with $i = 1, 2, 3$, where the subscripts u and s denote the unscaled and scaled sets. The 4p sets of Wachters [12] and Huzinaga [5] are [2p/2p], as in the cases of Cu and Cu_2.

The atomization energies (AEs) are defined by:

$$\mathrm{AE} = 13E(\mathrm{SCF:\ Cu\ \ atom}) - E(\mathrm{SCF:\ Cu_{13}}) \qquad (1)$$

where E(SCF) is the total energy calculated by the open-shell SCF method. The numerical results are shown in Table 9. The basis set without 4p functions gives a negative AE, whereas all the calculations with the valence 4p sets give a positive AE, demonstrating the importance of the valence 4p functions. The scaling on the valence 4p set increases the AE, especially for the [1p/3p] and [2p/3p] sets. Wachters [2p/2p], Huzinaga [2p/2p], and $[2p/3p]_{\mathrm{s}}$ sets give almost the same AEs (4.7 eV). The reason for this result is:

Table 6. SCF and CI total energies (in hartrees) for the Cu_2 molecule

R (bohrs)	4.0	4.4	4.8	5.2
SCF				
Present work	−3277.847786	−3277.858887	−3277.859457	−3277.855135
Huzinaga	−3277.847738	−3277.858829	−3277.859446	−3277.855136
Wachters	−3277.847753	−3277.858855	−3277.859449	−3277.855127
1-Reference CI[a]				
Present work	−3278.440526	−3278.446883	−3278.442559	−3278.433693
Huzinaga	−3278.439262	−3278.445712	−3278.441628	−3278.432781
Wachters	−3278.439732	−3278.446179	−3278.441994	−3278.433117
2-Reference CI[b]				
Present work	−3278.441299	−3278.447890	−3278.443949	−3278.435686
Huzinaga	−3278.441026	−3278.447808	−3278.444268	−3278.436245
Wachters	−3278.441521	−3278.448322	−3278.444695	−3278.436643
2-Reference CI with Davidson correction[c]				
Present work	−3278.500930	−3278.506491	3278.501482	−3278.492247
Huzinaga	−3278.500004	−3278.505784	−3278.501202	−3278.492206
Wachters	−3278.500655	−3278.506438	−3278.501751	−3278.492714

[a] CI dimensions are 63876, 55740, and 55740 for the present work, Huzinaga, and Wachters sets, respectively
[b] CI dimensions are 126844, 110670, and 110670 for the present work, Huzinaga, and Wachters sets, respectively
[c] See [30]

Table 7. Spectroscopic constants for the Cu_2 molecule[a]

	D_e (eV)	R_e (bohrs)	ω_e (cm^{-1})
SCF			
Present work	0.530	4.618	197
Huzinaga	0.527	4.620	196
Wachters	0.528	4.619	197
1-Reference CI			
Present work	0.529	4.400	236
Huzinaga	0.530	4.408	233
Wachters	0.527	4.405	234
2-Reference CI			
Present work	0.556	4.411	232
Huzinaga	0.587	4.426	227
Wachters	0.586	4.423	229
2-Reference CI with Davidson correction			
Present work	1.279	4.371	239
Huzinaga	1.301	4.385	235
Wachters	1.300	4.382	236
Exptl.[b]	2.05[c]	4.195	265

[a] See footnotes a, b, and c of Table 6
[b] See [32]
[c] D_e is estimated by $D_0(2.03\text{eV}) + \hbar\omega_e/2$ where $\hbar$ is the Planck constant

1. After scaling, the present work exponents read 0.41857, 0.13448, and 0.04803 and the latter two are close to those of Wachters [12] and Huzinaga [5].
2. In $[2p/3p]_s$ the contraction coefficient for the GTF with the exponent 0.13448 is much larger than that for the GTF with 0.41857 (see Table 3).

The two $[3p/3p]$ calculations, with and without scaling, give almost the same atomization energy. So far as we are concerned with energetics, the scaling is not essential for the uncontracted $[3p/3p]$ sets. In Table 10 we present GAOPs [35] for Cu in the Cu_4 planes, a corner Cu in Cu_5, and a central Cu in Cu_5 in the Cu_{13} (Cu_4-Cu_5-Cu_4) cluster. The $[1p/3p]$ and $[2p/3p]$ sets without the scaling factor show that the central Cu in Cu_5 is negatively charged, whereas for all the other $4p$ sets it is positively charged. The former calculations predict a positively charged ball on a surface of a negatively charged core for the Cu_{13} cluster, while the latter predict a negatively charged ball on a surface of a positively charged core. It is well known that Mulliken population analysis does not work well when the basis sets include diffuse functions. We feel the latter description is adequate for Cu_{13}. The orbital energies ε of the highest occupied orbitals and corresponding ionization energies (IEs) are collected in Table 11. The e_g orbital in the O_h symmetry is resolved into a_{1g} and b_{1g} orbitals in the D_{4h} symmetry. The calculations without valence $4p$ sets fail to generate molecular orbitals having the O_h symmetry, while the others successfully yield O_h-like orbitals. It suggests that the calculations without valence $4p$ sets may bring unexpected symmetry breaking. We also find that the ε and IE calculated with the unscaled $[1p/3p]_u$ and $[2p/3p]_u$ sets are little different from the corresponding values obtained with the scaled sets.

4 Conclusion

We developed GTF basis sets for $4p$ valence orbitals of the first-row transition metal atoms. Three primitive GTFs were used and they were determined to minimize the total energy of the excited configuration $4s^1 4p^1$. The test calculations were performed using the atom Cu, the diatom Cu_2, and clusters Cu_9 and Cu_{13}. From the

Table 8. Total energies *E* (in hartrees) for the ^1A_g ($^1\Sigma_g{}^+$) and $^1B_{1u}$ ($^1\Sigma_u{}^+$) states and excitation energies ΔE (in eV) from the ^1A_g ($^1\Sigma_g{}^+$) to the $^1B_{1u}$ ($^1\Sigma_u{}^+$) state of the Cu_2 molecule

		Present work	Huzinaga	Wachters	Exptl.[a]
1-Reference CI					
R_e (bohrs)	–	4.400	4.408	4.405	4.195
SCF	$E[^1B_{1u}\ (^1\Sigma_u{}^+)]$	−3277.767983	−3277.766612	−3277.766367	–
	$E[^1A_g\ (^1\Sigma_g{}^+)]$	−3277.858887	−3277.858918	−3277.858911	–
	ΔE	2.474	2.512	2.518	2.698
CI	$E[^1B_{1u}\ (^1\Sigma_u{}^+)]^b$	−3278.343110	−3278.341948	−3278.342350	–
	$E[^1A_g\ (^1\Sigma_g{}^+)]^c$	−3278.446883	−3278.445713	−3278.446179	–
	ΔE	2.823	2.824	2.825	2.698
2-Reference CI					
R_e (bohrs)	–	4.411	4.426	4.423	4.195
SCF	$E[^1B_{1u}\ (^1\Sigma_u{}^+)]$	−3277.768296	−3277.767120	−3277.766877	–
	$E[^1A_g\ (^1\Sigma_g{}^+)]$	−3277.859008	−3277.859106	−3277.859100	–
	ΔE	2.468	2.503	2.510	2.698
CI	$E[^1B_{1u}\ (^1\Sigma_u{}^+)]^d$	−3278.343286	−3278.342251	−3278.342647	–
	$E[^1A_g\ (^1\Sigma_g{}^+)]^e$	−3278.447885	−3278.447824	−3278.448334	–
	ΔE	2.846	2.873	2.876	2.698

[a] See [32]
[b] CI dimensions for $^1B_{1u}$ are 148396, 129390, and 129390 for the present work, Huzinaga, and Wachters sets, respectively
[c] CI dimensions for 1-reference ^1A_g are 63876, 55740, and 55740 for the present work, Huzinaga, and Wachters sets, respectively
[d] CI dimensions for $^1B_{1u}$ are the same as footnote b
[e] CI dimensions for 2-reference ^1A_g are 126844, 110670, and 110670 for the present work, Huzinaga, and Wachters sets, respectively

results for the atom and the diatom, we found that the present work uncontracted valence 4*p* sets always give the lowest total energies for the excited states irrespective of the states and the methods, indicating the adequacy of the set to describe the excited states including 4*p*-like excitations. The new set is suitable for high-quality molecular calculations including the excited states. It was also found that when we discuss the ground state of the clusters with a contraction, the introduction of the scaling factor is essential. We recommend the use of the present work set in the primitive form of [3*p*/3*p*].

Table 9. Total energies *E* (in hartrees) for the ground-state Cu and Cu_{13} and the atomization energies (AE, in eV)

Basis set	*E*(Cu)	*E*(Cu_{13})	AE
Without 4*p*	−1638.919314	−21305.89904	−1.416
Present work [1*p*/3*p*]$_u$	−1638.919576	−21306.08998	3.687
Present work [1*p*/3*p*]$_s$	−1638.919769	−21306.12447	4.557
Present work [2*p*/3*p*]$_u$	−1638.919777	−21306.11859	4.394
Present work [2*p*/3*p*]$_s$	−1638.919846	−21306.13018	4.685
Huzinaga [2*p*/2*p*]	−1638.919902	−21306.13149	4.701
Wachters [2*p*/2*p*]	−1638.919892	−21306.13220	4.724
Present work [3*p*/3*p*]$_u$	−1638.919896	−21306.13414	4.775
Present work [3*p*/3*p*]$_s$	−1638.920276	−21306.14079	4.822

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Table 10. GAOPs for the Cu_{13} ground state ($^6A_{1g}$)[a]

Basis set	Cu in Cu_4				Corner Cu in Cu_5				Center Cu in Cu_5			
	s	*p*	*d*	Total	*s*	*p*	*d*	Total	*s*	*p*	*d*	Total
Without 4*p*	6.99	12.00	9.98	28.97	6.84	12.00	9.98	28.82	7.80	12.00	10.12	29.92
Present work [*1p*/3*p*]$_u$	6.45	12.44	9.96	28.85	6.45	12.44	9.96	28.84	6.65	14.26	9.96	30.86
Present work [1*p*/3*p*]$_s$	6.76	12.35	9.96	29.07	6.76	12.35	9.96	29.07	5.47	12.74	9.95	28.17
Present work [2*p*/3*p*]$_u$	6.44	12.35	9.96	28.76	6.44	12.35	9.96	28.76	3.61	18.36	9.94	31.92
Present work [2*p*/3*p*]$_s$	6.87	12.29	9.95	29.12	6.87	12.29	9.95	29.11	5.33	12.27	9.95	27.55
Huzinaga [2*p*/2*p*]	6.89	12.39	9.95	29.24	6.96	12.41	9.95	29.32	5.30	10.58	9.93	25.80
Wachters [2*p*/2*p*]	6.85	12.37	9.95	29.17	6.95	12.39	9.95	29.29	5.42	11.10	9.93	26.45
Present work [3*p*/3*p*]$_u$	6.75	12.35	9.95	29.05	6.72	12.35	9.95	29.02	5.18	13.36	9.94	28.48
Present work [3*p*/3*p*]$_s$	6.91	12.34	9.95	29.20	6.90	12.34	9.95	29.19	5.40	11.36	9.92	26.68

Table 11. Orbital energies (ε) for the highest occupied a_{1g} and b_{1g} orbitals and corresponding ionization energies (IE, in hartrees)

Basis	a_{1g}		b_{1g}	
	ε	IE	ε	IE
Without 4*p*	−0.19543	0.18411	−0.17081	0.16434
Present work $[1p/3p]_\mathrm{u}$	−0.16683	0.15671	−0.16686	0.15640
Present work $[1p/3p]_\mathrm{s}$	−0.16402	0.15277	−0.16403	0.15234
Present work $[2p/3p]_\mathrm{u}$	−0.16619	0.15505	−0.16621	0.15462
Present work $[2p/3p]_\mathrm{s}$	−0.16529	0.15394	−0.16529	0.15347
Huzinaga $[2p/2p]$	−0.16518	0.15248	−0.16525	0.15201
Wachters $[2p/2p]$	−0.16519	0.15373	−0.16530	0.15331
Present work $[3p/3p]_\mathrm{u}$	−0.16571	0.15399	−0.16573	0.15351
Present work $[3p/3p]_\mathrm{s}$	−0.16524	0.15363	−0.16524	0.15315

References

1. Ditchfield R, Hehre WJ, Pople JA (1971) J Chem Phys 54: 724
2. Hehre WJ, Pople JA (1972) J Chem Phys 56: 4233
3. Tatewaki H, Huzinaga S (1979) J Chem Phys 71: 4339
4. Tatewaki H, Huzinaga S (1980) J Comput Chem 1: 205
5. Huzinaga S (ed) Gaussian basis sets for molecular calculations. Elsevier, Amsterdam
6. Schaefer A, Horn H, Ahrichs R (1992) J Chem Phys 97: 2571
7. Schaefer A, Huber C, Ahrichs R (1994) J Chem Phys 100: 5829
8. Tatewaki H, Koga T (1996) J Chem Phys 104: 8493
9. Tatewaki H, Koga T, Takashima H (1997) Theor Chem Acc 96: 243
10. Koga T, Tatewaki H, Matsuyama H, Satoh Y (1999) Theor Chem Acc 102: 105
11. Huzinaga S (1965) J Chem Phys 42: 1293
12. Wachters AJH (1970) J Chem Phys 52: 1033
13. Raffenetti RC (1973) J Chem Phys 58: 4452
14. Huzinaga S, Klobukowski M, Tatewaki H (1985) Can J Chem 63: 1812
15. Almloef J, Taylor PR (1987) J Chem Phys 86: 4070
16. Partridge H (1989) J Chem Phys 90: 1043
17. Huzinaga S, Miguel B (1990) Chem Phys Lett 175: 289
18. Almloef J, Taylor PR (1991) Adv Quantum Chem 22: 301
19. Dunning TH Jr (1989) J Chem Phys 90: 1007
20. Kendall RA, Dunning TH Jr (1992) J Chem Phys 96: 6796
21. Wood DE, Dunning Th Jr (1993) J Chem Phys 98: 1358
22. Wood DE, Dunning TH Jr (1993) J Chem Phys 99: 1914
23. Wood DE, Dunning TH Jr (1993) J Chem Phys 103: 4572
24. Pou-Amerigo R, Merchan M, Nebot-Gil I, Widmark P-O, Roos BO (1995) Theor Chim Acta 92: 149
25. Bauschlicher CW (1995) Theor Chim Acta 92: 183
26. Tatewaki H, Koga T (1997) Theor Chem Acc 101: 325
27. Roothaan CCJ, Bagus PS (1963) Methods Comput Phys 2: 47
28. Powell MJD (1964) Comput J 7: 155
29. Kuester JL, Mize JH (1973) Optimization techniques with Fortran. McGraw-Hill, New York, pp 331–343
30. Langhoff SR, Davidson ER (1976) J Chem Phys 64: 4469
31. Moore CE (1971) Atomic energy levels, vols 1 and 2. (NSRDS-NBS 35) National Bureau of Standards, Washington
32. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, vol IV: constants of diatomic molecules. Van Nostrand Reinhold, New York
33. Walch SP, Bauschlicher CW Jr, Langhoff SR (1986) J Chem Phys 85: 5900
34. Langhoff SR, Bauschlicher CW Jr, Walch SP, Laskowski B (1986) J Chem Phys 85: 7211
35. Mulliken RS (1955) J Chem Phys 23: 1833
36. Kashiwagi H, Takada T, Miyoshi E, Obara S, Sasaki F (1987) A library program of the Computer Center of the Institute for Molecular Science, Okazaki, Japan
37. Sasaki F, Sekiya M, Noro T, Ohtsuki K, Osanai Y (1993) In: Clementi E (ed) Methods and techniques in computational chemistry: METECC-94, vol A. STEF, Cagliari, p 115
38. Yamamoto S, Nagashima U, Aoyama T, Kashiwagi H (1988) J Comput Chem 9: 627
39. Diercksen GHF, Hall GG (1994) Comput Phys 8: 215