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Contracted Gaussian-type basis functions revisited.
III. Atoms K through Kr*

Toshikatsu Koga[1], Hiroshi Tatewaki[2], Hisashi Matsuyama[1], Yasuharu Satoh[1]

[1] Department of Applied Chemistry, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan
[2] Computation Center and Institute of Natural Sciences, Nagoya City University, Nagoya, Aichi 467-8501, Japan

Abstract. Six minimal basis sets of contracted Gaussian-type functions (GTFs) are developed for the third-row atoms K through Kr. The smallest and largest sets for transition metal atoms are (3333/33/3) and (8433/84/8), respectively, where a slash distinguishes the s, p, and d symmetries and single-digit figures in the parentheses denote the numbers of primitive GTFs. The two largest sets, (7433/74/7) and (8433/84/8), surpass the (62111111/33111/311) set of Schaefer et al. in the associated total energies. Our (8433/84/8) set is also superior to their (842111/631/411) set. The quality of the present basis sets is tested by self-consistent field (SCF) and configuration interaction (CI) calculations on the Cu_2 molecule. As the accuracy of the basis set increases, SCF calculations show a decrease in the dissociation energy and an increase in the equilibrium internuclear distance. The same tendencies are found in the results of CI calculations with and without a Davidson correction. All the present basis sets are freely available at the internet address: http://202.35.198.41/~htatewak/.

Key words: Contracted Gaussian-type basis sets – Third-row atoms – Cu_2 molecule

1 Introduction

For the first- and second-row atoms, many Gaussian-type function (GTF) basis sets have been developed. For heavier atoms, including the transition metal atoms, however, the number of available basis sets is comparatively small. GTF basis sets in the literature may be classified into three categories: the first applies primitive GTFs (PGTFs) to the description of self-consistent field (SCF) atomic orbitals (AOs), the second uses contracted GTFs (CGTFs), and the third employs a mixture of PGTFs and CGTFs. PGTF basis sets for the transition metal atoms include those developed by Wachters [1], Partridge [2], Huzinaga and Miguel [3], Huzinaga and Klobukowski [4], Pou-Amerigo et al. [5], and Bauschlicher [6], where the last two sets consist of natural orbitals obtained from configuration interaction (CI) calculations. Typical CGTF sets are those of Tatewaki and Huzinaga [7] and Huzinaga et al. [8]. Mixed basis sets were reported by Schaefer et al. [9, 10], where CGTFs and PGTFs are employed mainly for inner and outer shells, respectively. Recently, we have reported accurate minimal-type CGTF sets for the atoms Li through Ne [11] and Na through Ar [12], after careful reexamination of the CGTF sets given previously by Tatewaki and Huzinaga [7, 8]. We found insufficient optimality of the previous CGTF sets [7, 8], and suggested that refinements are desirable for the remaining atoms.

In the present paper, we report six minimal-type CGTF sets for the 18 third-row atoms from K to Kr. Because of its intimate connection with individual occupied AOs, the minimal-type basis set is useful to obtain good physical insights and perspectives, even when some CGTFs are decontracted into PGTFs in molecular applications. Three of the present CGTF sets for the first transition atoms, (3333/33/3), (4333/43/4), and (5333/53/5), are improved versions of the previous sets reported by Huzinaga et al. [8], while the remaining three sets, (6333/63/6), (7433/74/7), and (8433/84/8), are newly developed for more accurate molecular calculations, where single-digit figures in the parentheses indicate the numbers of PGTFs which span CGTFs and "/" separates the s, p, and d symmetries. In Sect. 2, our method of basis set determination is summarized. In Sect. 3, new basis sets are presented and compared with some literature sets. The present (7433/74/7) and (8433/84/8) sets will be shown to give total energies lower than the (62111111/33111/311) set of Schaefer et al. [9], and the present (8433/84/8) is better than their triple-zeta valence (TZV) (842111/631/411) set [10]. Section 4 tests the present basis sets in SCF and CI calculations of the Cu_2 molecule. Previously [11, 12], we recommended use of split-valence basis sets $(N21/(N-1)1)$ and $(N321/N21)$ with $N \geq 4$, respectively, for the first- and second-row atoms.

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Correspondence to: H. Tatewaki

For the first transition atoms, it will be shown that we should use a set with six or more d PGTFs, if the accuracy of first-row (421/31) and second-row (4321/421) is required.

2 Method of determination of basis sets

In their construction of the CGTF sets, Tatewaki and Huzinaga [7, 8] treated contraction coefficients in a CGTF as linear parameters and they used the Fock equation to determine the coefficients. The PGTF exponents are intrinsically nonlinear parameters. Tatewaki and Huzinaga determined the exponents by a repeated single-line search for individual exponents based on the presumed quadratic dependence of the total energy on them. Koga et al. [13, 14], however, pointed out in their studies on accurate Roothaan-Hartree-Fock wave functions that the coupled variation of exponents is significant for finding the optimum parameter set. In our construction of CGTF sets for the first- [11] and second-row [12] atoms, we found that nonlinear optimization is important for contraction coefficients and exponents in a coupled manner. The conjugate directions algorithm [15, 16] was sufficiently efficient to determine their optimum values with respect to the total energy. Nontrivial differences in the previous and present optimization methods can be exemplified for the Cu atom described by the smallest (3333/33/3) set: the total energy of the original Huzinaga set [8] is -1631.637982 hartrees, while that of the present set is -1631.648027 hartrees. The energy improvement amounts to 0.01 hartrees, supporting the view that the present optimization is more powerful than the previous one.

3 Basis sets for third-row atoms

In the present study, we have developed CGTF sets $(N333/N3/N)$ with $N = 3$–6 and $(N433/N4/N)$ with $N = 7$ and 8 for the atoms Sc to Zn. The corresponding sets for the K and Ca atoms exclude a CGTF for the $3d$ AO, and those for the atoms Ga to Kr include an additional CGTF with three PGTFs for the $4p$ AO. We use symbols $\#N$ to label these basis sets, where $N(= 3$–8) stands for the number of PGTFs of the first CGTF. Analogous notation will also be used to refer to the CGTF sets reported previously [11, 12] for the first- and second-row atoms. Tabulated in Table 1 are the total energy errors ΔE of the third-row CGTF sets relative to the numerical Hartree-Fock (NHF) values [17]. In the smallest $\#3$ and largest $\#8$ sets, ΔE varies form 2.737 (K atom) to 10.808 hartrees (Kr atom) and from 0.008 to 0.028 hartrees, respectively, across the third row. If we compare the ratio of the maximum and minimum errors for the respective sets, the present six sets are classified into two groups: for the smaller four sets $\#3$ through $\#6$, the ratio is about 4.0, while for the larger two sets $\#7$ and $\#8$ it is about 3.6. The reduced error ratio across the period in the larger two sets originates mainly from better descriptions of the $2s$ and $3p$ orbitals in the vicinity of the nucleus. We similarly found [12] for Al to Ar that the (743/74) set gives a lower total energy than the (833/74) set.

The accuracy of the outer orbital energies reflects the quality of the orbital shape in a valence region which becomes important in a molecular environment. For the three symmetries, the orbital energy errors $\Delta\varepsilon_i$ of the outermost AOs relative to the NHF values [17] are given in Fig. 1 for the basis sets $\#N$ with $N = 4$–8. The errors $\Delta\varepsilon_{4s}$ are roughly 1/10 times smaller than $\Delta\varepsilon_{3p}$ and $\Delta\varepsilon_{3d}$, and the errors $\Delta\varepsilon_{4p}$ for the atoms Ga-Kr are much smaller than $\Delta\varepsilon_{3p}$ because of an extra p CGTF corresponding the $4p$ AO. The $\Delta\varepsilon_{3d}$ is largest for Cu, as observed in other minimal basis calculations (see for example [18]). Previously [11], we showed that for the first-row atoms, the errors $\Delta\varepsilon_{2p}$ of $\#4$, the (43/4) set, for the valence $2p$ AO lie between 2.2 and 17.8 millihartrees. Fr the second-row atoms, $\Delta\varepsilon_{3p}$ of $\#4$ were found [12] to be 0.4–3.8 millihartrees. For the atoms Sc through Kr, the errors $\Delta\varepsilon_{3d}$ of $\#5$ are 2.0–23.8 millihartrees and those of $\#6$ are 0.3–7.9 millihartrees. When these valence er-

Table 1. SCF total energy errors relative to NHF values for the third-row atoms. All values in hartrees

Z	Atom	NHF	#3	#4	#5	#6	#7	#8
19	K	−599.1647868	2.737154	0.642043	0.179921	0.066098	0.017189	0.007865
20	Ca	−676.7581859	3.018366	0.707553	0.199007	0.073983	0.018756	0.008529
21	Sc	−759.7357180	3.352838	0.786209	0.221406	0.082708	0.020741	0.009427
22	Ti	−848.4059970	3.713874	0.870631	0.245268	0.091917	0.022871	0.010400
23	V	−942.8843377	4.103229	0.961615	0.270887	0.101729	0.025161	0.011446
24	Cr	−1043.356376	4.606108	1.084635	0.305442	0.114020	0.028385	0.012914
25	Mn	−1149.866252	4.969492	1.163722	0.327470	0.123172	0.030219	0.013757
26	Fe	−1262.443665	5.458202	1.278781	0.359680	0.135216	0.033074	0.015041
27	Co	−1381.414553	5.979069	1.401202	0.393825	0.147904	0.036102	0.016403
28	Ni	−1506.870908	6.535125	1.531961	0.430209	0.161332	0.039321	0.017844
29	Cu	−1638.963742	7.315715	1.729400	0.486284	0.180549	0.044589	0.020125
30	Zn	−1777.848116	7.755412	1.818858	0.509724	0.190407	0.046338	0.020972
31	Ga	−1923.261010	8.203672	1.912233	0.534788	0.200719	0.047742	0.021280
32	Ge	−2075.359734	8.683518	2.016120	0.563875	0.212959	0.049997	0.022238
33	As	−2234.238654	9.185707	2.126848	0.595389	0.226315	0.052568	0.023396
34	Se	−2399.867612	9.707422	2.242843	0.628726	0.240584	0.055393	0.024730
35	Br	−2572.441333	10.248483	2.364063	0.663843	0.255716	0.058397	0.026168
36	Kr	−2752.054977	10.808241	2.490130	0.700602	0.271674	0.061567	0.027706

Fig. 1a–c. Outermost orbital energy errors from K through K$_r$ relative to the NHF values: **a** 4s orbital; **b** 3p or 4p orbital; **c** 3d orbital
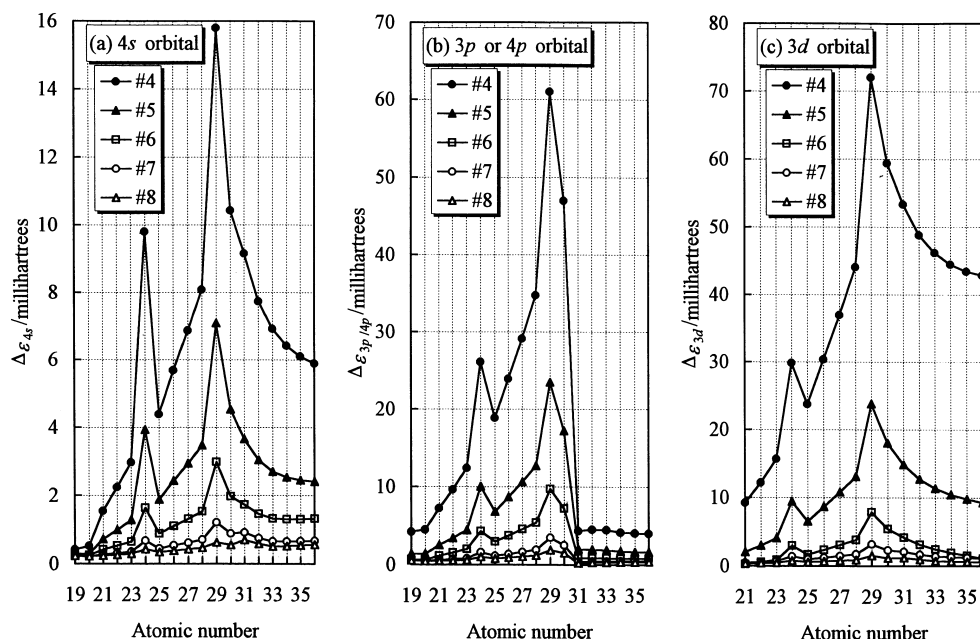
rors are compared, the third-row #5 set is slightly worse than the first-row #4 set, and the third-row #6 set worse than the second-row #4 set. It was pointed out [11] that, for the first-row atoms, split-valence derivatives of #4 such as (421/31) are the smallest reliable sets for molecular calculations. Then, the above errors in the valence orbital energies suggest that derivatives of #6 would be the smallest molecular sets for systems with third-row atoms.

For the 2s, 4s, 3p, and 3d AOs of the copper atom, Fig. 2 depicts errors $\Delta R_i(r)$ in the atomic radial functions $R_i(r)$ of the present #4, #6, #7, and #8 sets relative to the NHF functions. The second innermost 2s AO is added in the figure to demonstrate the significance of increased s PGTFs in the basis set accuracy, as mentioned before. We find that the errors are commonly large for $r \leq 0.1$ bohr and sharply decrease with an increasing number of PGTFs which describe an inner region. It is convenient to introduce labels Sk, Pk, and Dk to specify the kth CGTFs of the s, p, and d symmetries. In Fig. 2a we find that increased PGTFs in S1 reduces $\Delta R_{2s}(r)$ around the nucleus. An addition of a PGTF to S2 improves $R_{2s}(r)$, especially in the region $0.0003 \leq r \leq 0.02$ bohrs. Figure 2b also shows that an enlarged S2 also reduces the errors in the outermost 4s radial function in the region $0.0004 \leq r \leq 0.1$ bohrs. In Fig. 2c we see an additional PGTF in P2 improves the 3p AO for $0.001 \leq r \leq 0.1$ bohrs. Figure 2d shows that the increased d PGTFs in D1 reduces $\Delta R_{3d}(r)$ for $0.01 \leq r \leq 0.2$ bohrs. All these observations indicate that added PGTFs are mainly used to improve the radial functions in the region where the 1s AO distributes. In fact, the 1s AO has the mean radius $\langle r \rangle = 0.053$ bohrs and contains 1.85 electrons in a sphere with the radius $r = 0.1$ bohrs. In addition to appropriate behavior in the valence region, we thus see that the ability to describe properly the interaction between 1s and other electrons (including another 1s electron) is also important for high-quality basis sets.
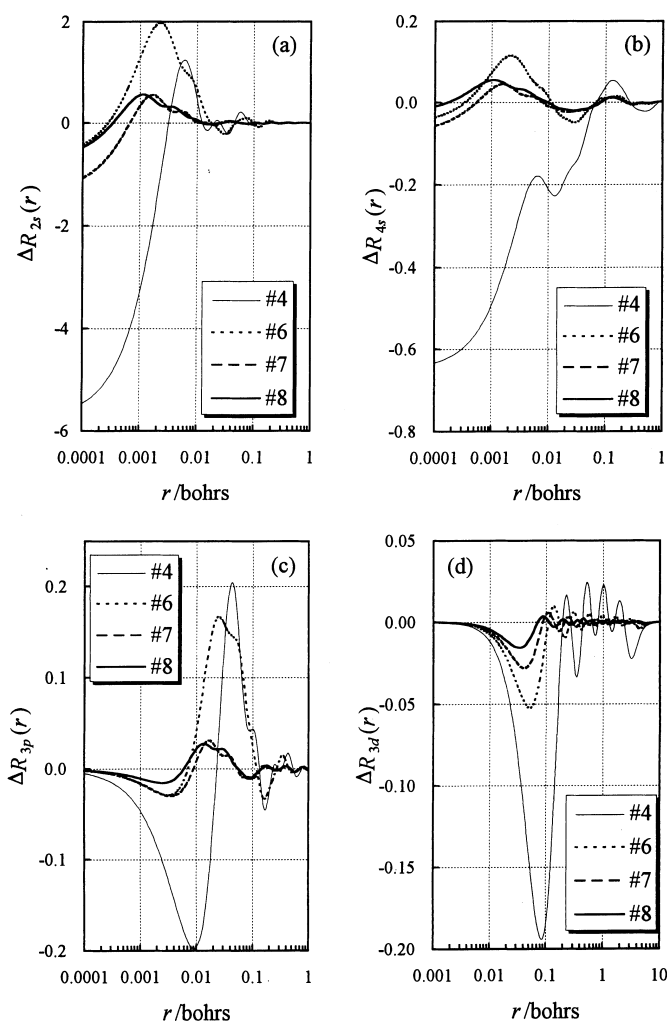
Fig. 2a–d. Errors in atomic radial functions in the #N CGTF sets with $N = 4$–8 for the Cu atom relative to the NHF functions: **a** 2s orbital; **b** 4s orbital; **c** 3p orbital; **d** 3d orbital

We have computed SCF total energies of the Cu atom in its ground ^2S state, using JAMOL [19], MICA [20], and GAMESS [21] programs. Note that the first two programs use five members for d GTFs, whereas the last uses six members. The results from the present and some literature [3, 4, 9, 10, 22–24] basis sets are compared in Table 2. Some derived sets, generated by decontracting an outer CGTF of minimal-type #N sets and adding some polarization/diffuse functions, have been also examined and their decontraction schemes are explicitly given in the table by using the number of PGTFs. In Table 2, $+2p$ means an addition of two Huzinaga et al.'s p-type polarization functions [8], $+2p'$ an addition of two Wachters' p-type polarization functions [1] modified by a scale factor $\sqrt{1.25}$ [22], and $+1d$ an addition of a Hay's diffuse d-type function [25]. The present #6 set gives a total energy close to that of Wachters' $(62111111/5112/311) + 2p' + 1d$ and the present #7 set gives an energy lower than that of Schaefer et al.'s $(62111111/33111/311)$ set. We note that the six-membered GTFs give a lower total energy than the five-membered GTFs by 2 millihartrees even for the $(84321/84/311111) + 2p$ set. For our molecular tests we have also examined a large GTF set [3, 4] composed of $(23,23,23,23,111/13,13,1111/71111111)$, which will be called the reference (ref) GTF set hereafter. The ref set has an SCF total energy of -1638.963687 hartrees in a five-membered d calculation, which is only 0.06 millihartrees above the NHF value and is 20 millihartrees below the present #8 value.

4 Molecular tests

4.1 SCF calculations

The Cu$_2$ molecule in its ground $^1\Sigma_g^+$ state has been chosen for our test of the quality of the new CGTF basis sets. At the internuclear distance $R = 4.4$ bohrs, for example, the largest $(84321/84/311111) + 2p$ set in the present test gives a total energy of -3277.9091 hartrees, while the energy of the smallest $(43321/43/211) + 2p$ set lies above this by about 3.3 hartrees. A large Slater-type function (STF) set, $12s8p6d + 2p + 1d + 3f + 1g$, gave -3277.9453 hartrees at the same distance [24], and the energy was considered to be close to the Hartrees-Fock (HF) limit. Since the difference in the two corresponding atomic calculations is 0.0348 hartrees for two Cu atoms (see Table 2), the difference between the two molecular calculations (0.0362 hartrees) is acceptable. A detailed table of SCF (and CI) total energies is available upon request to H.T. at the internet address htatewak@cc.nagoya-cu.ac.jp for various GTF basis sets at a few R values examined in this study.

The spectroscopic constants calculated with several basis sets are summarized in Table 3. The table has two groups of entries, one from five-membered d calculations and the other from six-membered d calculations. The present largest set with five-membered d calculations predicts a dissociation energy D_e of 0.48 eV, an equilibrium internuclear distance R_e of 4.62 bohrs, and a vibrational frequency ω_e of 197 cm^{-1}. The ref $+ 2p$ set gives $D_e = 0.49$ eV, $R_e = 4.61$ bohrs, and $\omega_e = 197$ cm^{-1} in a six-membered d calculation. All these values are close enough to the near HF limit results obtained in the above-mentioned STF calculations [24]:

Table 2. SCF total energies (in hartrees) of the Cu atom in its ground ^2S state

Basis sets	Five-membered d	Six-membered d
Present basis sets and their derivatives		
#3	-1631.648027	
#4	-1637.234342	
$(43321/43/211) + 2p$	-1637.240084	-1637.292322
#5	-1638.477458	
$(53321/53/2111) + 2p$	-1638.479242	
$(53321/53/311) + 2p' + 1d$	-1638.488146	-1638.501156
#6	-1638.783193	
$(63321/63/3111) + 2p$	-1638.784137	
$(63321/621/3111) + 2p$	-1638.784744	
#7	-1638.919153	
$(74321/74/4111) + 2p$	-1638.919891	
$(74321/74/31111) + 2p$	-1638.919891	
#8	-1638.943617	
$(84321/84/5111) + 2p$	-1638.944288	
$(84321/84/41111) + 2p$	-1638.944288	-1638.945994
$(84321/84/311111) + 2p$	-1638.944288	-1638.946253
Literature basis sets		
$(62111111/5112/311) + 2p' + 1d$[a]	-1638.817697	-1638.818838
$(62111111/51111/4111) + 1p$[b]	-1638.8635	
$(62111111/33111/311)$[c]	-1638.904562	
$(842111/631/411)$[d]	-1638.919163	
Reference GTF[e]	-1638.963687	
Reference GTF[e] $+ 2p$		-1638.963695
Slater-type functions[f]	-1638.9637	
Numerical Hartree-Fock[g]	-1638.963742	

[a] [22]
[b] [23]
[c] [9]
[d] [10]
[e] $(23,23,23,23,111/13,13,1111/ 71111111)$ set from [3, 4]
[f] [24]
[g] [17]

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Table 3. Calculated spectroscopic constants for the Cu_2 molecule

Basis sets	SCF			CI without Davidson correction			CI with Davidson correction		
	D_e (eV)	R_e (bohrs)	ω_e (cm^{-1})	D_e (eV)	R_e (bohrs)	ω_e (cm^{-1})	D_e (eV)	R_e (bohrs)	ω_e (cm^{-1})
Five-membered d calculations									
(43321/43/211) + 2p	1.105	4.360	232	1.582	4.218	257	2.148	4.183	262
(53321/53/2111) + 2p	0.663	4.549	206	0.907	4.410	233	1.491	4.377	239
(53321/53/311) + 2p′ + 1d	0.553	4.570	204	0.702	4.437	231	1.287	4.411	237
(63321/63/3111) + 2p	0.533	4.601	201	0.695	4.466	231	1.287	4.436	237
(63321/621/3/311) + 2p	0.538	4.602	201						
(62111111/5112/311) + 2p′ + 2p′ + 1d[a]	0.534	4.575	203						
(62111111/5112/311) + 2p′ + 2p′ + 1d[b]	0.52	4.62	201						
(62111111/51111/4111) + 1p[c]				1.211	4.409	228			
(74321/74/4111) + 2p	0.494	4.616	198	0.634	4.479	228	1.226	4.451	234
(74321/74/31111) + 2p	0.495	4.615	198						
(84321/84/5111) + 2p	0.484	4.616	197	0.628	4.479	226	1.213	4.452	232
(84321/84/41111) + 2p	0.484	4.616	197						
(84321/84/311111) + 2p	0.484	4.616	197						
Six-membered d calculations									
(43321/43/211) + 2p	1.123	4.330	230	1.635	4.151	256	2.310	4.102	263
(53321/53/311) + 2p′ + 1d	0.556	4.567	205	0.669	4.408	233	1.351	4.372	240
(62111111/5112/311) + 2p′ + 2p′ + 1d[a]	0.535	4.573	203	0.620	4.412	230	1.328	4.374	237
(84321/84/41111) + 2p	0.485	4.616	197	0.566	4.454	225	1.266	4.416	232
(84321/84/311111) + 2p	0.486	4.614	197	0.565	4.454	228	1.265	4.415	232
Reference GTF[d] + 2p	0.494	4.614	197	0.560	4.420	228	1.295	4.376	235
Slater-type functions[e]	0.52	4.62	189						
Experimental	2.05	4.195	265	2.05	4.195	265	2.05	4.195	265

[a] [22]
[b] [31]
[c] [23]
[d] (23,23,23,23,111/13,13,1111/71111111) set from [3, 4]
[e] [24]
[f] The zero point energy is excluded from the value given in [30]

$D_e = 0.52$ eV, $R_e = 4.62$ bohrs, and $\omega_e = 189$ cm^{-1}. It was also reported [24] that a $12s\ 8p\ 6d + 2p + 1d$ STF set, which compares with the $ref + 2p$ set, gives $D_e = 0.50$ eV. We therefore anticipate that a further incorporation of polarization functions with higher angular moment will not essentially change the spectroscopic constants obtained from the present largest set with two p-type polarization functions.

From Table 3 we see that basis set superposition errors (BSSEs) [26–29] for the $(43321/43/211) + 2p$ and $(53321/53/2111) + 2p$ sets are 0.61 and 0.17 eV, respectively. The basis sets including six d PGTFs, namely $(53321/53/311) + 2p' + 1d$, $(62111111/5112/311) + 2p' + 1d$, and $(63321/63/3111) + 2p$, still give BSSEs of 0.06, 0.04, and 0.04 eV, respectively. However, the sets including seven d PGTFs do not essentially have a BSSE. In a previous paper for the first-row atoms [11], we showed that SCF calculations with $(421/31) +$ polarization functions, such as $2d + 1f$, are almost free from BSSEs. The third-row $(63321/63/3111)$ set is little worse in quality than the $(421/31)$ set for B to Ne, so far as prediction of a correct D_e is concerned. The SCF calculations with six-membered d GTFs give results parallel to those of five-membered d GTFs.

4.2 CI calculations

We have performed CI calculations with single and double excitations (SDCI) from SCF valence molecular orbitals. For all the basis sets examined, CI calculations lower total energies by 0.45–0.50 hartrees from the corresponding SCF values. Inclusion of electron correlation generally increases D_e and ω_e but decreases R_e, as shown in Table 3. As a result, the constants R_e and ω_e from CI calculations are closer to the experimental values [30] than those from SCF calculations.

However, there remains a large difference between the CI and experimental D_e values: even large basis sets having six or more d PGTFs add only a small amount (0.1–0.2 eV) of energy to SCF D_e values, and the resultant CI D_e values (0.56–0.70 eV) are still far from the experimental value 2.05 eV [30]. We note that the present calculation with $(62111111/5112/311) + 2p' + 1d$ gives a D_e of 0.62 eV, which is about half of the 1.21 eV reported by Walch et al. [31]. We suspect that Walch et al. adopted the triplet $7\sigma_g 7\sigma_u$ state at $R = 50$ bohrs as the dissociation limit to calculate D_e [32].

For the atoms B to Ne [11] and Al to Ar [12], we showed that basis sets suitable for molecular calculations give nearly the same molecular extra correlation energies as a large reference basis set. The BSSEs in SCF calculations are retained also in CI calculations, and an error in the CI D_e is enhanced by the same amount of an error in the SCF D_e. In the present analysis of new CGTF sets for third-row atoms, we employed the $ref + 2p$ results as a reference for six-membered d calculations, but the $(84321/84/5111) + 2p$ results for five-membered d calculations because we could not perform CI calculations with the $ref + 2p$ set owing to program limitations and because the two sets are expected to give similar spectroscopic constants at the CI level. In five-membered d CI

calculations, D_e from $(84321/84/5111) + 2p$ is 0.63 eV, while the values from $(43321/43/211) + 2p$ and $(53321/53/2111) + 2p$ are 1.58 and 0.91 eV, indicating BSSEs of 0.95 and 0.28 eV, respectively. The BSSEs are enhanced in CI calculations compared with those (0.61 and 0.17 eV) of SCF calculations, showing again the inadequacy of these sets for molecular calculations. The CI BSSEs for $(53321/53/311) + 2p' + 1d$ and $(63321/63/3111) + 2p$ are both 0.07 eV, and are nearly the same as their SCF values. The BSSE with $(74321/74/4111)$ in CI is negligibly small. These results are essentially unaltered in CI calculations with six-membered d functions.

At an internuclear distance around R_e, a Davidson correction [33] to the total energy of the Cu_2 system was small (0.03–0.06 hartrees) for any basis set. The spectroscopic constants from CI calculations with a Davidson correction are also summarized in Table 3. The D_e values given by five- and six-membered d calculations with $(43321/43/211) + 2p$ are 2.15 and 2.31 eV, which are close to the experimental value [30] at first glance. However, BSSEs in the above two calculations are found to be 0.94 and 1.02 eV, respectively. Thus the accidental agreement between the calculated and experimental D_e values is brought about by a BSSE. For the $(53321/53/2111) + 2p$ set, the BSSE still amounts to 0.28 eV in a five-membered d calculation. These results suggest that introduction of a Davidson correction neither reduces nor enhances BSSEs in CI calculations. The D_e values obtained by CI calculations with a Davidson correction are 1.2–1.4 eV for larger sets. These values are roughly twice those of CI calculations without a Davidson correction. This implies that higher excitations are necessary for an accurate prediction of D_e. According to the studies of Bauschlicher et al. [22] and Walch et al. [31], on the other hand, addition of higher angular momentum polarization functions hardly improves D_e. The D_e values calculated with higher order excitations were summarized by Pettersson and Åkeby [34] and the best value quoted by them is 1.73 eV.

The electron correlation effect on the chemical bond can be measured by the molecular extra correlation energy $E_c^{extra}(R)$ defined by

$$E_c^{extra}(R) \equiv E_c^{mol}(R) - 2E_c^{atom}$$

for a homonuclear diatomic system, where $E_c^{mol}(R)$ and E_c^{atom} are molecular and atomic correlation energies, respectively. In Fig. 3 we plot $E_c^{extra}(R)$ of some CGTF sets (without a Davidson correction) as a function of the internuclear distance R. In five-membered d GTF calculations, six basis sets, namely $(43321/43/211) + 2p$, $(53321/53/2111) + 2p$, $(53321/53/311) + 2p' + 1d$, $(63321/63/3111) + 2p$, $(74321/74/4111) + 2p$, and $(84321/84/5111) + 2p$, were examined, and in six-membered d GTF calculations, six basis sets, namely $(43321/43/211) + 2p$, $(53321/53/311) + 2p' + 1d$, $(62111111/5112/311) + 2p' + 1d$, $(84321/84/41111) + 2p$, $(84321/84/311111) + 2p$, and $ref + 2p$ were also examined. For all the cases, the behavior of $E_c^{extra}(R)$ around R_e is approximately linear and increases with increasing R. Then, the molecular extra correlation contributes to shorten the calculated R_e in CI more than in SCF, as seen
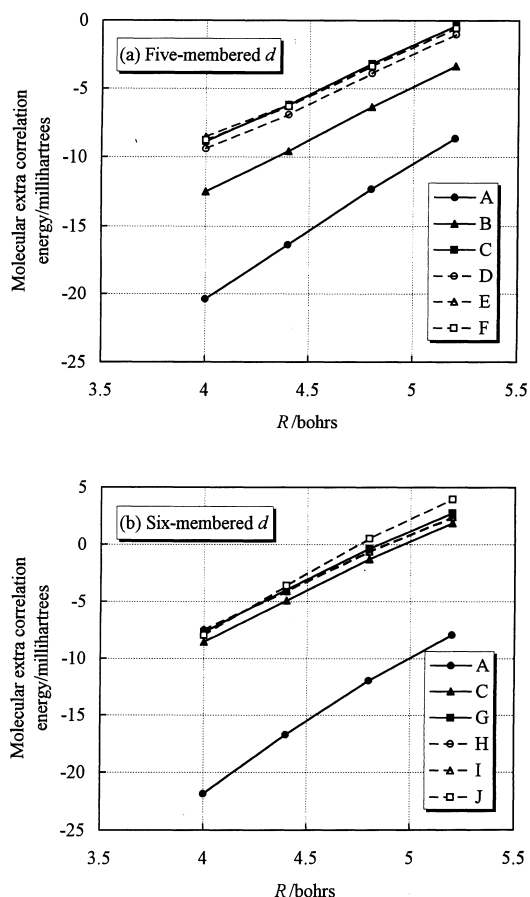
Fig. 3a,b. Molecular extra correlation energies in Cu_2 system around R_e. **a** Five-membered d GTF calculations: A (43321/43/211) + 2p; B (53321/53/2111) + 2p; C (53321/53/311) + 2p' + 1d; D (63321/63/3111) + 2p; E (74321/74/4111) + 2p; and F (84321/84/5111) + 2p. **b** six-membered d GTF calculations: A (43321/43/211) + 2p; C (53321/53/311) + 2p' + 1d; G (62111111/5112/311) + 2p' + 1d; H (84321/84/41111) + 2p; I (84321/84/311111) + 2p; and J ref + 2p

in Table 3. In the five-membered d calculations given in Fig 3a, the $E_c^{\text{extra}}(R)$ lines are almost superimposable for the four sets (53321/53/311) + 2p' + 1d and larger, but those for (43321/43/2111) + 2p and (53321/53/2111) + 2p sets are exceptionally large in magnitude owing to BSSEs, which lead to an exaggerated D_e. In Fig. 3b we again observe a wrong $E_c^{\text{extra}}(R)$ for the (43321/43/211) + 2p set in six-membered d calculations.

5 Summary

Six minimal-type CGTF basis sets have been developed for the third-row atoms K to Kr. For the first transition atoms, the total energy of the present (6333/63/6) set is close to that of Wachters' (62111111/5112/311) set [1]. The (7433/74/7) set surpasses the (62111111/33111/311) set of Schaefer et al. [9] and is quite close to their TZV (842111/631/411) set [10]. The total energy of the largest (8433/84/8) set is lower than that of the TZV set and is above the NHF value by 7.9–27.7 millihartrees. The present CGTF

sets have been tested using the Cu_2 molecule at SCF and CI levels. Both five- and six-membered d basis calculations have been compared. The Cu_2 results have suggested that the ($N333/N3/N$) set and its split-valence modifications with $N \leq 5$ are not appropriate for a large BSSE, and the (6333/63/6) set and its derivatives are smallest CGTF sets for reliable molecular calculations. Larger basis sets derived from (7433/74/7) and (8433/84/8) are suitable for calculations of higher quality.

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