Bull. Chem. Soc. Jpn., **68**, 1915—1919(1995)

Segmented Contractions of Gaussian Basis Sets for Relativistic Molecular Calculations

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(Received March 3, 1995)

A method for segmented contractions of relativistic Gaussian basis sets is proposed, in which the large- and the small-component coefficients of the contracted basis sets are taken directly from the uncontracted relativistic basis sets and their kinetic balance is disregarded. The energy increases by this contraction scheme are found to be very small and the variational collapse does not occur. This method also reproduces very well the orbital energies and the radial expectation values of uncontracted basis sets. Examples of calculations on iodine (Z=53), gold (Z=79), and thorium (Z=90) are reported in detail.

In *nonrelativistic* atomic and molecular calculations using basis-set expansion method two kinds of contraction schemes of Gaussian basis sets are used, i. e., the segmented contraction$^{1)}$ and the general contraction.$^{2)}$ There are merits and demerits in both kinds of the contractions.

In *relativistic* calculations both kinds of the contraction schemes have also been adopted. For example, the segmented contaction is employed in Ref. 3 and the general contraction in Refs. 4 and 5. However, the details about how to perform the contractions do not seem established, since the relativistic calculations are new as compared to the nonrelativistic ones.

For the segmented contractions of relativistic Gaussian basis sets one of the present authors (O. M.) proposed$^{6)}$ (hereafter referred to as I) a method which consists of the following steps. First, using the nonrelativistic Gaussian basis sets one forms the segmented basis sets of large components. Second, one generates the corresponding small-component basis sets by the kinetic balance (KB) scheme$^{7)}$ to guarantee that the basis sets will give proper kinetic energies in the nonrelativistic limits. Third, if the basis sets thus formed gave large increase of the total energies, one decontracts the contracted basis functions that contain primitive functions of large exponent parameters (EP). It seems essential for this method to adopt the third step which leaves the basis functions of large EPs uncontracted. Unless one adopts it, one encounters the large energy increase or even the variational collapse.

However, Ishikawa$^{8)}$ showed examples in which one could contract the basis functions of large EPs. He adopted for large components the contracted basis sets fully optimized nonrelativistically$^{9,10)}$ and generated the small-component basis sets using KB scheme. In contrast to the results obtained by the method of I, his calculations gave small energy increases and did not show any variational collapse. The reasons why the contracted basis sets adopted by him gave good results would be the facts that the basis sets for the large components were fully optimized nonrelativistically, so that the large-component together with the KB generated small-component basis sets led to proper cancellation of the kinetic and the potential energies in the nonrelativistic limits and the relativistic corrections were made by other uncontracted basis functions contained in the relativistic basis sets.

Thus, his examples would suggest a scheme for segmented contractions of the relativistic basis sets: One performs nonrelativistic calculations to get the large-component contracted basis sets, whose EPs as well as the contraction coefficients are fully optimized and then obtains the corresponding small-component basis sets by the KB. However, optimization of the contraction coefficients is expensive even in nonrelativistic calculations since they are treated$^{10)}$ as non-linear parameters as the EPs. Thus, we tried to find other simpler contraction schemes and have found a method.

In this new method we simply take the contraction coefficients of both the large and the small components from the relativistic basis sets computed in uncontracted forms and disregard the KB between them. Compared to the previous method$^{6)}$ this method gives considerably better total energies and does not show any variational collapse. It also gives better orbital energies and other physical quantities such as the radial expectation values. In this paper we report examples of calculations on iodine (Z=53), gold (Z=79), and thorium (Z=90).

Calculations and Results

Since the relativistic effect is small and we should use high-quality basis sets for relativistic calculations, we contracted only the basis functions of large EPs which describe the inner parts of orbitals and left uncontracted those of smaller EPs which describe the outer parts of orbitals. We examined the effects of contractions on the total energies, the orbital energies, and the radial expectation values. In this paper we report only the results of iodine (Z=53), gold (Z=79) as in I and also those of thorium (Z=90).

For each atom we first performed the Dirac–Fock–Roothaan calculations using uncontracted Gaussian functions and then employed the coefficients of the lowest orbitals (i. e., $1s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, etc.) for the contracted basis sets. We disregarded the KB between the large and the small components of the contracted basis functions, although we retained it for the primitive basis functions. Atomic nuclei were assumed to be uniformly charged spheres[11)] whose radii were calculated using atomic masses 127, 197, and 232 for iodine, gold, and thorium. The speed of light was taken to be 137.037 au.

Iodine. As in I, Stromberg et al.'s[12)] nonrelativistic basis sets were augmented with two s-type and two p-type primitive basis functions. This augmented (17s13p6d) basis set in uncontracted form gave a total energy higher than the Dirac–Fock limit[11)] by 0.83 au and was taken the reference. We employed various sizes of the segmented contractions to see how much energy would be lost when the contractions were done. Table 1 shows some of the calculated total energies. In order to see the effect of the contractions of the basis sets of s-symmetry species the 1s basis set of size 7 was gradually made uncontracted, the basis functions of other symmetry species being left uncontracted. Calculations Nos. 2—5 are examples of these contractions. When we compare the results of calculation No. 2 with calculations Nos. 3—5, we see that the decontractions of basis functions of smaller EPs in this contracted basis function improve the total energy considerably. Similar calculations were done for the p contractions (calculations Nos. 6—9) and d contractions (calculations Nos. 10—12). In these calculations it is also seen that the decontractions of the basis functions of small EPs in the contracted basis sets improve the energy appreciably.

Thus, using the contractions employed in calculations Nos. 3, 8, and 11, calculation No. 14 was done, which was of double-zeta quality. Similar calculations (Nos. 13 and 15) were done to see the effect of different contraction sizes. It is observed that the energy increase of the s, p, d contractions (calculations Nos. 13—15) is approximately the sums of independent contributions from each symmetry species. For example, the energy increase of calculation No. 14 (=0.08249 au) is the sum of calculations Nos. 3, 8, and 11 (=0.08250 au). This is also observed in the method of I.

In the previous method[6)] we had to leave uncontracted the primitive basis functions of large EPs, while in the present method we could put them into a contracted basis function. The energy increases due to the contractions are thus considerably smaller than those of

Table 1. Effect of Contractions on Total Energies of Iodine

Calculation No.	Contraction	Total energy	Energy increase
Uncontracted			
1	$(1^{17}/1^{13}/1^{6})$	−7114.96108	0
s contracted			
2	$(7,1^{10}/1^{13}/1^{6})$	−7114.59366	0.36742
3	$(5,2,1^{10}/1^{13}/1^{6})$	−7114.90678	0.05429
4	$(6,1,1^{10}/1^{13}/1^{6})$	−7114.93219	0.02889
5	$(5,1,1,1^{10}/1^{13}/1^{6})$	−7114.96001	0.00107
p contracted			
6	$(1^{17}/6,1^{7}/1^{6})$	−7114.77921	0.18187
7	$(1^{17}/5,1,1^{7}/1^{6})$	−7114.92839	0.03269
8	$(1^{17}/4,2,1^{7}/1^{6})$	−7114.93928	0.02180
9	$(1^{17}/4,1,1,1^{7}/1^{6})$	−7114.95925	0.00182
d contracted			
10	$(1^{17}/1^{13}/4,1^{2})$	−7114.33912	0.62195
11	$(1^{17}/1^{13}/3,1,1^{2})$	−7114.95457	0.00641
12	$(1^{17}/1^{13}/2,1,1,1^{2})$	−7114.96099	0.00009
s, p, d contracted			
13	$(5,2,1^{10}/4,2,1^{7}/4,1^{2})$	−7114.26272	0.69836
14	$(5,2,1^{10}/4,2,1^{7}/3,1,1^{2})$	−7114.87859	0.08249
15	$(5,1,1,1^{10}/4,1,1,1^{7}/2,1,1,1^{2})$	−7114.95810	0.00298

All values in au.

method of I. For example, although exact comparison is not possible, the $(1^5,2,1^{10}/1^4,2,1^7/3,1^3)$ basis set of method of I gave an energy increase of 0.2770 au, while the $(5,2,1^{10}/4,2,1^7/3,1^3)$ basis set of the present method (calculation No. 14) gave an increase of 0.0825 au. In the method of I the energy increases of s and p contractions are found larger than those of d contractions, while in the present method the increases are irrespec-

Table 2. Effect of Contractions on Total Energies of Gold

Calculation No.	Contraction	Total energy	Energy increase
Uncontracted			
1	$(1^{20}/1^{16}/1^{10}/1^5)$	−19034.6918	0
s contracted			
2	$(8,2,1^{10}/1^{16}/1^{10}/1^5)$	−19031.7492	2.9426
3	$(6,2,2,1^{10}/1^{16}/1^{10}/1^5)$	−19033.5187	1.1731
4	$(8,1,1,1^{10}/1^{16}/1^{10}/1^5)$	−19033.9261	0.7657
5	$(6,2,1,1,1^{10}/1^{16}/1^{10}/1^5)$	−19034.6852	0.0066
p contracted			
6	$(1^{20}/8,2,1^6/1^{10}/1^5)$	−19029.5955	5.0963
7	$(1^{20}/6,2,2,1^6/1^{10}/1^5)$	−19030.9124	3.7794
8	$(1^{20}/6,2,1,1,1^6/1^{10}/1^5)$	−19034.6794	0.0125
d contracted			
9	$(1^{20}/1^{16}/5,1^5/1^5)$	−19034.6821	0.0097
s, p, d contracted			
10	$(6,2,1^{12}/6,2,1^8/5,1^5/1^5)$	−19034.6631	0.0288
s, p, d, f contracted			
11	$(6,2,2,1^{10}/6,2,1^8/5,1^5/3,2)$	−19033.4967	1.1951
12	$(6,2,1,1,1^{10}/6,2,1^8/5,1^5/3,2)$	−19034.6631	0.0288

All values in au.

Table 3. Effect of Contractions on Total Energies of Thorium

Calculation No.	Contraction	Total energy	Energy increase
Uncontracted			
1	$(1^{24}/1^{19}/1^{16}/1^8)$	−26510.5634	0
s contracted			
2	$(8,1^{16}/1^{19}/1^{16}/1^8)$	−26510.3288	0.2354
3	$(7,1,1^{16}/1^{19}/1^{16}/1^8)$	−26510.5320	0.0314
4	$(6,2,1^{16}/1^{19}/1^{16}/1^8)$	−26510.5600	0.0033
p contracted			
5	$(1^{24}/7,2,1^{10}/1^{16}/1^8)$	−26510.5100	0.0533
6	$(1^{24}/5,2,2,1^{10}/1^{16}/1^8)$	−26510.5110	0.0523
7	$(1^{24}/8,1,1^{10}/1^{16}/1^8)$	−26510.5171	0.0462
8	$(1^{24}/6,2,1,1^{10}/1^{16}/1^8)$	−26510.5580	0.0054
d contracted			
9	$(1^{24}/1^{19}/6,1^{10}/1^8)$	−26510.5594	0.0039
10	$(1^{24}/1^{19}/3,3,1^{10}/1^8)$	−26510.5619	0.0015
s, p, d contracted			
11	$(6,2,1^{16}/8,1^{11}/6,1^{10}/1^8)$	−26510.5099	0.0535
12	$(6,2,1^{16}/6,2,1^{11}/6,1^{10}/1^8)$	−26510.5507	0.0127
s, p, d, f contracted			
13	$(6,2,1^{16}/6,2,1^{11}/6,1^{10}/3,1^5)$	−26510.5507	0.0127

All values in au.

tive of the s, p, or d contractions.

Gold. As in I Gropen's[13] nonrelativistic basis set was augmented with one s-type and two p-type primitive basis functions. This augmented (20s16p10d5f) basis set gave a total energy higher than the Dirac–Fock limit[11] by 0.781 au and was taken as the reference. Table 2 shows the effect of the contractions on the total energies. The same kinds of calculations as for the iodine were done and similar results were obtained. We find that the f-contraction has negligible effect when we compare the calculated results of No. 10 with No. 12. This is due to the fact that in gold there is only one f orbital for each $f_{5/2}$ and $f_{7/2}$ symmetry species and the effect of its contraction is almost independent of other symmetry species as was observed in the case of s, p, d contractions of iodine (calculation Nos. 13—15 of Table 1.

Thorium. Recently Minami and Matsuoka[14] generated relativistic Gaussian basis sets of radon through plutonium. They were obtained by fitting to the numerical Dirac–Fock wave functions.[11] We report the calculations on thorium ($Z=90$) using this basis set. This (24s19p16d8f) basis set in uncontracted form gave a total energy higher than the Dirac–Fock limit[11] by 0.11326 au and was taken as the reference. The same kinds of calculations were done as for the iodine and the gold. Table 3 shows the effect of the contractions on the total energies. Similar results were obtained as for the iodine and the gold.

Table 4 compares the orbital energies and the radial expectation values of the contracted basis set (calculation No. 13) with those of the reference uncontracted basis sets (calculation No. 1). The effect of the contractions are very small; it is gratifying that the lower orbital energies and $\langle 1/r \rangle$ expectation values do not change appreciably in spite of the contractions.

Discussion and Conclusion

In the present method, the contraction coefficients of both the large and the small components are taken directly from the relativistic basis sets computed in uncontracted forms. Thus the KB between them are disregarded, which means that the present basis sets might not give proper kinetic energies in the nonrelativistic limits and would lead to the variational collapse. However, the present and other calculations hitherto performed using this new method have given considerably better energies and physical quantities than those computed using the method of I and have not shown the variational collapse if unreasonably large sizes of contractions were not made. In the method of I the basis functions of large EPs were left uncontracted, while in

Table 4. Orbital Energies ϵ and Radial Expectation Values $\langle 1/r \rangle$ and $\langle r \rangle$ of Thorium Calculated Using Uncontracted and Contracted (Calculation No. 13 of Table 3) Basis Sets

Orbital	$-\epsilon_{\mathrm{ref}}$	$-\epsilon$	$\langle 1/r \rangle_{\mathrm{ref}}$	$\langle 1/r \rangle$	$\langle r \rangle_{\mathrm{ref}}$	$\langle r \rangle$
$1s_{1/2}$	4.05851D+3	4.05851D+3	.117805D+3	.117804D+3	.141037D−1	.141037D−1
2	7.58566D+2	7.58567D+2	.296559D+2	.296581D+2	.584457D−1	.584457D−1
3	1.93114D+2	1.93115D+2	.108266D+2	.108273D+2	.151925D+0	.151925D+0
4	5.01948D+1	5.01950D+1	.462100D+1	.462118D+1	.331314D+0	.331314D+0
5	1.15681D+1	1.15682D+1	.200568D+1	.200573D+1	.702136D+0	.702135D+0
6	2.06581D+0	2.06583D+0	.846212D+0	.846226D+0	.155900D+1	.155900D+1
7	2.09329D−1	2.09332D−1	.291902D+0	.291905D+0	.430473D+1	.430469D+1
$2p_{1/2}$	7.29879D+2	7.29881D+2	.295660D+2	.295660D+2	.475289D−1	.475289D−1
3	1.80131D+2	1.80130D+2	.107214D+2	.107223D+2	.143067D+0	.143069D+0
4	4.43470D+1	4.43468D+1	.450924D+1	.450951D+1	.330387D+0	.330388D+0
5	9.24947D+0	9.24939D+0	.189629D+1	.189635D+1	.733202D+0	.733206D+0
6	1.31722D+0	1.31721D+0	.755542D+0	.755553D+0	.173276D+1	.173276D+1
$2p_{3/2}$	6.03585D+2	6.03588D+2	.222035D+2	.222035D+2	.574432D−1	.574432D−1
3	1.50893D+2	1.50894D+2	.878733D+1	.878747D+1	.160875D+0	.160875D+0
4	3.67149D+1	3.67150D+1	.386698D+1	.386702D+1	.364922D+0	.364921D+0
5	7.50610D+0	7.50613D+0	.166721D+1	.166721D+1	.807879D+0	.807880D+0
6	1.00165D+0	1.00166D+0	.659091D+0	.659094D+0	.194959D+1	.194959D+1
$3d_{3/2}$	1.30310D+2	1.30311D+2	.866976D+1	.866979D+1	.139142D+0	.139141D+0
4	2.73248D+1	2.73246D+1	.367775D+1	.367740D+1	.363187D+0	.363195D+0
5	3.98141D+0	3.98135D+0	.144488D+1	.144479D+1	.913533D+0	.913545D+0
6	2.22746D−1	2.22738D−1	.423285D+0	.423269D+0	.303535D+1	.303540D+1
$3d_{5/2}$	1.24358D+2	1.24359D+2	.826958D+1	.826961D+1	.144440D+0	.144440D+0
4	2.59021D+1	2.59022D+1	.353830D+1	.353868D+1	.373884D+0	.373886D+0
5	3.71859D+0	3.71858D+0	.139351D+1	.139360D+1	.941380D+0	.941385D+0
6	2.10444D−1	2.10441D−1	.404482D+0	.404485D+0	.316174D+1	.316177D+1
$4f_{5/2}$	1.35351D+1	1.35353D+1	.324834D+1	.324835D+1	.366948D+0	.366947D+0
$4f_{7/2}$	1.31771D+1	1.31772D+1	.319602D+1	.319603D+1	.372324D+0	.372323D+0

Quanties for the uncontracted basis set are marked with suffix 'ref'. All values in au.

the present method they could be contracted so that the total number of basis functions could be effectively reduced. The present method is a natural extension of the contraction scheme adopted in nonrelativistic calculations where the contraction coefficients are taken from those of the uncontracted basis sets.

In conclusion, the previously proposed method⁶⁾ for segmented contractions of relativistic Gaussian basis sets could be replaced with the present method in most calculations.

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