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Comments on relativistic basis sets

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Abstract. Adding the tight and diffuse Gaussian-type functions (GTFs), Faegri's variationally determined double-zeta-quality basis sets for molecular relativistic calculations are examined. An example atom is Cm. When the tight s-type GTF is added the total energy increases, whereas when diffuse GTFs are added the total energy decreases. The reasons for these findings are clarified. It is also pointed out that not only the Faegri's sets but also other variationally determined basis sets would show similar behavior so far as the expansion terms are not sufficient.

Keywords: Relativistic basis sets – Gaussian – Variational collapse – Prolapse – Cm and CmF_x

In line with the development of heavy-element chemistry, the number of molecular orbital calculations for lanthanoid atoms and even actinoid atoms, in which the relativistic Hamiltonian terms are of special importance, is increasing. In such studies, suitable basis set for the relativistic Hamiltonian must be employed. Here, the Dirac–Fock–Roothaan (DFR) [1] method is used as the standard all-electron four-component relativistic recipe. There are three types of basis sets for DFR calculations:

1. The large nonrelativistic basis set, which could be used directly as a relativistic set [2, 3].
2. The large nonrelativistic basis set with modification for the relativistic Hamiltonian [4] (see later).
3. Sets that are optimized energetically [5, 6, 7, 8].

We study type 3 in some detail. Dyall [5] obtained a Gaussian-type-function (GTF) set with double-zeta-quality for the 4p, 5p, and 6p elements, where the l^- and l^+ exponents are restricted to have the same values. Faegri [6] gave GTF sets of the same quality as Dyall [5] for K(19) to Uno(118), imposing the further restrictions that the s, d, and g primitive GTFs (pGTFs) share the same exponents and the p, f, and h share another. These are called the family sets. Koga, Tatewaki, and Matsuoka (KTM) [7] developed the set from H(1) to Xe(54) in which the pGTF exponents for l^+ and l^- are fully optimized. The quality of the set is high. These authors [8] also developed the sets for Cs(55)–Hg(80).

Recently, we have been making DFR calculations on curium fluorides (CmF_x). Initially, we tried Faegri's set [6] for the Cm atom in primitives, which should reduce the computational costs owing to its common exponents. However, we found slow convergence and the intrusion of positronic eigenvalues which is often caused by a poor description of the wavefunctions near the nucleus. We therefore preferred a type 2 basis set [4], although the computations were harder. We found the numbers of the intrusion decrease considerably. We show the characteristics of two basis sets [4, 6] and investigate their "robustness" in molecular environments.

In this work, we employed a Gaussian nucleus model where the nucleus radius was taken, following Visscher and Dyall [9], as

$$R = (2.03952714A^{1/3} + 1.39058668) \times 10^{-5}\,\mathrm{bohr} \ ,$$

where A is a mass number. The average energy of the configuration [10] is used throughout the paper.

Later we see the effects of additional diffuse and tight pGTFs on these basis sets. First we discuss the effect of the diffuse pGTFs. Seven sets were used, as follows. TM1: the nonrelativistic sets of Koga, Tatewaki, and Shimazaki (KTS) [11]. TM2: modified KTS (MKTS) [4] generated by replacing seven s and one p pGTFs of KTS with those of hydrogenic ion DFR, and adding those five p and one d. TM3: MKTS plus 7s′(rpl) with two Gaussians for the $7s$ spinor replaced [4]. TM4: TM3 plus two diffuse p Gaussians ($\zeta = 0.05616$ and 0.02246). F1: the relativistic sets of Faegri [6]. F2:F1 plus diffuse one s. F3:F2 plus two p GTFs ($\zeta = 0.0677$ and 0.0251). The DFR total energies for Cm $5f^87s^2$ are shown in Table 1 Although the expansion terms are smaller, the Faegri set and its derivative give lower DFR total energy values

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Table 1. Dirac–Fock–Roothaan (*DFR*) total energies (hartree) for Cm $5f^{8}7s^{2}$ by various basis and energy-lowering (millihartree) relative to TM4 or F1 for Cm $5f^{8}7s^{2}$. The Koga, Tatewaki, and Shimazaki (*KTS*) set for the large component is composed of 28s, 21p, 18d, and 13f primitive Gaussian-type functions (*GTFs*) and is denoted as 28s21p18d13f

Basis name	Expansion terms	$5f^{8}7s^{2}$	ΔE
TM1: KTS	28s21p18d13f	−31323.047120	1709.706
TM2: MKTS	28s26p19d13f	−31324.756629	0.197
TM3: MKTS + 7s'(rpl)	28s26p19d13f	−31324.756826	0.000
TM4: TM3 + two diffuse p	28s28p19d13f	−31324.756858	−0.032
TM5: TM4 + tight s	29s28p19d13f	−31324.762673	−5.847
F1: Faegri (family)	25s21p17d12f	−31324.766323	0.000
F2: F1 + diffuse s	26s21p17d12f	−31324.766443	−0.120
F3: F2 + two diffuse p	26s23p17d12f	−31324.766597	−0.274
F4: F1 + tight s	26s21p17d12f	−31324.760676	5.647
NDF (Visscher and Dyall)		−31324.793171	

Table 2. Spinor energies (hartree) for Cm $5f^{8}7s^{2}$

	$1s$	$2s$	$2p^{-}$	$2p^{+}$
TM2: MKTS	−4748.1209	−908.6214	−876.5222	−702.1728
TM3: MKTS + 7s'(rpl)	−4748.1202	−908.6208	−876.5216	−702.1722
TM4: TM3 + two diffuse 7p	−4748.1203	−908.6209	−876.5217	−702.1722
TM5: TM4 + tight s	−4748.1226	−908.6213	−876.5217	−702.1723
F1: Faegri (family)	−4748.1313	−908.6267	−876.5288	−702.1768
F2: F1 + diffuse s	−4748.1325	−908.6279	−876.5300	−702.1780
F3: F2 + two diffuse p	−4748.1328	−908.6281	−876.5303	−702.1783
F4: F1 + tight s	−4748.1291	−908.6263	−876.5289	−702.1768
NDF (Visscher and Dyall [a])	−4748.1319	−908.6283	−876.5336	−702.1786

[a] See Ref. [9]

than the KTS, MKTS, and MKTS derivatives. To see the influences of the added diffuse GTFs, the DFR total energy of TM4 relative to that of TM3 which is considered to be a standard relativistic KTM basis for actinoid atoms and that of F2 and F3 relative to F1 are also shown in Table 1. The diffuse two p GTFs in TM4 lower the DFR total energies by only 0.03 mhartree, whereas those in F3 cause a reduction of 0.15 mhartree. A similar energy-lowering is found for the diffuse s of Faegri. The energy-lowering in the Faegri derivatives is significantly larger than that in the MKTS derivatives. If exponent optimization works properly in the relativistic calculations, the energy lowering in Faegri plus diffuse sp should be smaller than or similar to values for MKTS plus diffuse sp. Inappropriate couplings of the large and small components in the smaller sets often cause a very large total energy-lowering (variation collapse) [1, 12, 13, 14, 15, 16, 17, 18] and the inappropriate couplings in the larger sets give a smaller total energy-lowering, called a prolapse [6]. The larger energy-lowerings of the diffuse GTFs on F1 suggest that the exponent variation tightens even the outer charge cloud through the coupling terms of the two components. The vector space spanned by F1 may incline to an inaccurate direction. Next we discuss the effects of a tight s.

Since a variation collapse or a prolapse is ordinarily considered as originating from the poor description of the spinors near the nucleus, addition of the tight s GTFs to the set (F1) may lead to higher DFR total energies. We add a tight s to TM4 and F1 to generate TM5 and F4, where the ratio of the innermost two s GTFs of the respective sets is used to determine the tight s exponent. The results are also included in Table 1. Inclusion of the GTF largely pushed up the Faegri set DFR total energies (F4) but not the energies for the MKTS derivative (TM5). Furthermore if we add the TM5 tight s to F1, we obtain −31324.759861 hartree, which is 6.462 mhartree higher than the total energy of F1. Inversely if we add an F4 tight s to TM4, the total energy is −31324.763663 hartree and the energy-lowering relative to TM4 is −6.837 mhartree. Probably addition of any tight single s pGTF to F1 leads to a higher DFR total energy. The innermost spinor energies for $5f^{8}7s^{2}$ are compared in Table 2. In F1 (Faegri), the $1s$ spinor energy is close to that for numerical Dirac–Fock (NDF). The diffuse s and p GTFs in Faegri derivatives reduce the $1s$ spinor energy below that for NDF through the improvement of $1s$ outer-shell interactions, indicating the F1 $1s$ spinor energy is too low. On the other hand, the tight s increases it, suggesting again the inadequacy of the inner-shell description. To close this paragraph we compare the first seven exponents of the F1(Faegri) and TM2 (MKTS) sets in Table 3. We recall that in TM2, these exponents are those of Cm^{95+}.

Table 3. Comparison of the seven innermost s exponents for Cm $5f^{8}7s^{2}$

	F1(Faegri)	M2(MKTS)
s1	$5.438186507 \times 10^{7}$	$4.407308900 \times 10^{7}$
s2	$1.406923438 \times 10^{7}$	$1.166148700 \times 10^{7}$
s3	$4.555919983 \times 10^{6}$	$3.926199200 \times 10^{6}$
s4	$1.597609222 \times 10^{6}$	$1.450345400 \times 10^{6}$
s5	$5.965879208 \times 10^{5}$	$5.764630700 \times 10^{5}$
s6	$2.317303337 \times 10^{5}$	$2.387048700 \times 10^{5}$
s7	$9.303663137 \times 10^{4}$	$1.023570700 \times 10^{5}$

Table 4. Cm DFR total energies with and without ghost orbitals and energy difference between these (hartree). The atomization energy (AE) is calculated relative to Cm($f^7d^1s^2$)

$CmF_2/Cm^{+2}(f^7s^1)$		
MKTS		
CmF_2 R_{Cm-F} 4.0077 bohr, AE 9.958 eV		
$Cm^{+2}(f^7s^1)$ + two F-ghost	TE	ΔE
TM6: TM4 + 2g/D_{2h}[a]	−31324.125168	0.0
TM7: TM6 + F-ghost/D_{2h}[a]	−31324.125271	−0.000103
Faegri		
CmF_2 R_{Cm-F} 4.0075 bohr, AE 9.953 eV		
$Cm^{+2}(f^7s^1)$ + two F-ghost		
F5: F3 + 3g/D_{2h}[a]	−31324.131474	0.0
F6: F5 + F-ghost/D_{2h}[a]	−31324.131938	−0.000464
$CmF_3/Cm^{+3}(f^7)$		
MKTS		
CmF_3 R_{Cm-F} 3.9595 bohr, AE 15.066 eV		
$Cm^{+3}(f^7)$ + three F-ghost		
TM6: TM4 + 2g/C_{2v}[a]	−31323.435632	0.0
TM7: TM6 + F-ghost/C_{2v}[a]	−31323.435711	−0.000079
Faegri		
CmF_3 R_{Cm-F} 3.9599 bohr, AE 15.057 eV		
$Cm^{+3}(f^7)$ + two F-ghost		
F5: F3 + 3g/C_{2v}[a]	−31323.441801	0.0
F6: F5 + F-oghost/C_{2v}[a]	−31323.442360	−0.000559

[a] The molecule is assumed to have D_{8h} symmetry for CmF_2 and D_{3h} symmetry for CmF_3, but the calculations were performed using D_{2h} and C_{2v}, respectively

Nevertheless the first five exponents of F1 are larger than those of TM2. From what was discussed at the end of the previous paragraph and just above, we can say that exponent variations for the F1 set make the whole the charge distribution tight. We suspect all the variationally determined sets more or less suffer from variation collapse or prolapse especially for the heavier atoms.

Actual molecular calculations are, however, less stringent than those just described. We have tested the MKTS and Faegri derivatives, using ghost F sets placed with an optimized geometry of F_2 and F_3 units of CmF_2 and CmF_3 having molecular symmetry, $D_{\infty h}$ and D_{3h}. In molecular and ghost calculations, two and three g pGTFs are added respectively to TM4 and F3. These are TM6 with (28s28p19d13f2g) and F5 with (26s23p17d12f3g). The set for fluorine was 12s8p [7] augmented with diffuse 1s, 1p, and 3d pGTFs (totally 13s9p3d), where the geometric average of exponents for l^- and l^+ was used. The atomic states calculated were $Cm^{2+}(f^7s^1)$ for CmF_2 and $Cm^{3+}(f^7)$ for CmF_3. The DFR total energies calculated with and without ghosts are shown in Table. 4. The two Cm basis sets give almost the same bond length and atomization energy for these molecules. However, the energy-lowering with the Faegri derivative set by including the ghosts is 5–7 times larger than that in the MKTS derivative set, suggesting that this set is a little soft compared to MKTS, even in molecular environments.

In conclusion the sets developed by Faegri give a more contracted charge distribution than what is expected for the true Dirac–Hartree–Fock. This probably leads to slow convergence in self-consistent-field calculations and intrusion of positronic eigenvalues when the basis set is used in primitives. We are also afraid that the variation collapse (prolapse) arises more often when the inner-core excitations are treated. This comment holds for any variationally determined basis sets unless the sets are expanded with sufficient pGTFs.

The program used for the atomic calculations was atomic DFR [19], and DIRAC [20] was used for molecular calculations. All the calculations were performed on the computing facilities of the Japan Atomic Energy Research Institute, the Japan Science and Technology Corporation, and Nagoya City University. The present investigation was performed as part of the Earth Simulator project promoted by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and was partly supported by a Grant-in-Aid for Scientific Research by MEXT.

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