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Fully relativistic prolapse-free Gaussian basis sets: The actinides and $_{81}$Tl–$_{88}$Ra

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Among the heaviest elements, the actinides have been among the most fascinating and challenging elements for computational chemistry.[1] Quantum chemical calculations on these elements must include relativistic effects and the most accurate way of including these effects is through the four-component Dirac equation.[2]

Central in the four-component calculations is the analytic approximation where one-electron functions are expanded in a finite basis set of Gaussian basis functions. It is known for some time that the four-component basis set expansion, or Dirac–Fock–Roothan (DFR) method, often meets variation collapse,[3,4] which results in a calculated DFR total energy lower than the corresponding numerical value. When Faegri developed four-component family sets,[5] he found a small variation collapse and called it prolapse. The prolapse, for instance, can be understood as an instability due to poor description of spinors near the nucleus and becomes more critical as Z increases.[5,6] The inconvenience with prolapse is that it may cause convergence problems[7] in the self-consistent-field (SCF) procedure, may lead to wrong results[8] or may interfere into the value of dissociation energy in four-component correlated calculations.[9]

Although much effort has been made by Faegri,[5,10] Dyall,[11] and Koga, Tatewaki and Koga[12] in developing four-component basis sets for the heavier elements, all these basis sets are not explicitly prolapse-free. One of us worked on an universal basis set[13] where the prolapse test[6] was performed for some representative elements ($_{102}$No, $_{86}$Rn, $_{80}$Hg, $_{70}$Yb, $_{56}$Ba) and since the prolapse test was not performed explicitly in all elements covered here, we can only guess that it would be prolapse-free. There are a scarce number of prolapse-free basis sets in literature and this is especially true for actinides.

To our knowledge, there is only one explicit prolapse-free basis set for the actinides and for elements from $Z=81$ up to $Z=89$. Yamamoto *et al.*[14] developed a very accurate prolapse-free basis set for actinides recently, but it has the drawback of being very large in size: the recommended set is (64,64,64,46,46,46,46) and the practical set is (56,48,48,36,36,36,36) in terms of $(s^+,p^-,p^+,d^-,d^+,f^-,f^+)$ symmetries, respectively. Another drawback is that they cannot be used into popular four-component codes such as DIRAC04 (Ref. 15) due to different sets for p^- and p^+, d^- and d^+, and f^- and f^+.

In this short paper, we report relativistic basis sets for actinides and elements from $_{81}$Tl up to $_{89}$Ra that are prolapse-free for practical purposes. The method used here to generate the basis sets has been described previously[16] in our paper for basis sets from $_{103}$Lr up to $_{118}$Uuo: All calculations were performed with the atomic relativistic program written by Matsuoka and Watanabe[17] with the Gaussian model as suggested by Visscher and Dyall.[18] In this Gaussian nuclear model, the root mean square (RMS) can be approximately related to atomic mass and exponential parameter ξ by empirical formulas,[18] so one can derive both the RMS and the ξ given the atomic mass and use all basis sets reported here in four-component codes such as DIRAC04 and/or MOLFDIR.

The idea is to obtain basis sets where the absolute values of the energy difference between the Dirac–Fock–Roothan (DFR) total energy E(DFR) and the corresponding numerical value[18] E(NDF) are at a millihartree order of magnitude and sufficiently compact in size to restrain the prolapse to be smaller than (or close to) 1 mH (approximately 0.6 kcal/mol) when it occurs, resulting in a good balance between cost and accuracy.

Table I summarizes the DFR total energies E(DFR) in hartrees, their errors ΔE relative to the numerical E(NDF) values $[\Delta E=E(\mathrm{DFR})-E(\mathrm{NDF})]$ in millihartrees, basis set size (GTFs), and the variation of the energy in millihartrees due to addition of a single tight S function (ΔS_+, prolapse test[6,19]). Also given in Table I are the electronic configuration for each element and its atomic mass value used to derive the corresponding exponential parameter ξ.

Our basis sets have almost half of the number of GTFs compared to the available prolapse-free basis sets in literature[14] for these elements. The largest ΔE was found to $_{85}$At (6.70 mH or 4.26 kcal/mol), the smallest for the $_{87}$Fr (1.81 mH or 1.14 kcal/mol) and for all elements the prolapse is lower or close to 1 mH. For the actinides, with the exception of Pa and U, the prolapse is negligible (at order of 10^{-5} H). Compared to values of an explicit non-prolapse-free basis set where the prolapse test is available,[12,6] our basis sets are much more stable, accurate, and reliable. Our new basis sets, in addition to the fact that are explicit prolapse-free, are also smaller and have similar quality of ΔE values at millihartree order of magnitude when compared with the previous universal set.[13]

A MICROSOFT EXCEL spreadsheet with the Gaussian ex-

TABLE I. Atomic numbers, atoms, electronic configurations, atomic mass, basis set size (GTFs), total energy E(DFR), energy difference (ΔE in millihartrees) between numerical and basis set total values, and variation of energy [$\Delta(S_+)$, the prolapse test, in millihartrees] due to addition of a single S tight Gaussian function (all values are in a.u. unless otherwise indicated).

								Other work[a,b]	
Z	Atom	Configuration	Atomic mass	GTFs	E(DFR)	ΔE	$\Delta(S_+)$	ΔE[a]	$\Delta(S_+)$[b]
81	Ti	[Hg]$6p^1$	205	$26s22p16d11f$	−20274,844219	6.43	0.00	−0.39	+5.78
82	Pb	[Hg]$6p^2$	208	$27s22p16d12f$	−20913,708330	6.00	+0.23	−0.95	+6.54
83	Bi	[Hg]$6p^3$	209	$26s22p16d11f$	−21565,700310	5.77	+0.46	−1.50	+7.36
84	Po	[Hg]$6p^4$	209	$26s22p16d11f$	−22231,007219	5.96	+0.50	−2.07	+8.25
85	At	[Hg]$6p^5$	210	$26s22p16d11f$	−22909,800826	6.79	+0.66	−2.72	+9.27
86	Rn	[Hg]$6p^6$	222	$29s26p16d12f$	−23602,101920	2.33	+0.91	−3.71	+10.65
87	Fr	[Rn]$7s^1$	223	$29s26p16d12f$	−24308,191538	1.81	+0.03	−5.16	+11.86
88	Ra	[Rn]$7s^2$	226	$29s24p16d12f$	−25028,184839	2.97	+0.87	−6.51	+13.39
89	Ac	[Rn]$7s^25f^1$	227	$31s26p17d12f$	−25762,365795	2.24	0.00	−8.08	+15.03
90	Th	[Rn]$7s^25f^2$	232	$31s26p17d12f$	−26510,905222	2.19	+0.03	−9.66	+16.98
91	Pa	[Rn]$7s^25f^26d^1$	231	$32s26p17d12f$	−27274,376118	2.69	+1.03	−10.90	+19.00
92	U	[Rn]$7s^25f^36d^1$	238	$31s26p17d12f$	−28052,834289	5.67	+1.18	−12.89	+21.56
93	Np	[Rn]$7s^25f^46d^1$	237	$32s26p17d12f$	−28846,999641	6.45	+0.01	−14.80	+24.10
94	Pu	[Rn]$7s^25f^6$	244	$32s26p17d13f$	−29656,615169	2.34	0.00	−16.86	+27.32
95	Am	[Rn]$7s^25f^7$	243	$31s25p17d12f$	−30482,620759	3.40	+0.07	−19.35	+30.55
96	Cm	[Rn]$7s^25f^8$	247	$32s26p17d12f$	−31324,787967	5.20	+0.01	−22.83	+34.42
97	Bk	[Rn]$7s^25f^86d^1$	247	$32s26p17d12f$	−32183,770490	n/a[c]	+0.02	n/a[c]	+38.54
98	Cf	[Rn]$7s^25f^{10}$	251	$32s26p17d12f$	−33059,717957	4.33	+0.02	−29.45	+43.41
99	Es	[Rn]$7s^25f^{11}$	252	$32s26p17d12f$	−33953,150704	4.61	+0.02	−33.62	+48.66
100	Fm	[Rn]$7s^25f^{12}$	257	$32s26p17d12f$	−34864,095765	5.28	+0.02	−38.62	+54.89
101	Md	[Rn]$7s^25f^{13}$	258	$32s26p17d12f$	−35793,437961	5.94	+0.02	−43.93	+61.54
102	No	[Rn]$7s^25f^{14}$	259	$32s26p17d12f$	−36741,348670	4.06	+0.02	−49.89	+68.97

[a]Total energy differences taken from Ref. 12.
[b]Prolapse energy variations taken from Ref. 6. ΔE difference is not shown for $_{97}$Bk because the electronic configuration [Rn]$7s^25f^9$ adopted by Visscher and Dyall (Ref. 18) is different from configuration adopted in this work and from Yamamoto *et al.* (Ref. 14), [Rn]$7s^25f^86d^1$.
[c]Not available.

ponents and a summary of all calculations can be downloaded as supplementary material.[20]

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[20] See EPAPS Document No. E-JCPSA6-129-612835 for the EXCELL spreadsheet with Gaussian basis sets for actinides. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.