



# Gaussian basis set of triple zeta quality for atoms Fr through Lr: Application in DFT calculations of molecular properties

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## Introduction

Segmented all-electron Gaussian basis sets of triple zeta quality plus polarization functions (TZP) and the corresponding augmented sets (ATZP) for the elements Fr to Lr were generated using non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonians [1,2]. In the past, similar qualities sets were constructed for the elements from H to La and Hf to Rn [3-7].

To assess the performance of these small size all-electron basis sets, at the DKH-B3LYP level, bond lengths, dissociation energies, polarizabilities and first atomic ionization energies of a sample of diatomics were calculated for Fr–Ac [1], and for the remaining elements, bond distances, dissociation energies, natural charges and populations of the valence orbitals of the actinides monoxides were calculated [2] with the B3LYP/TZP-DKH procedure. The B3LYP/ATZP-DKH static mean dipole polarizabilities were also computed [2] for Am and No. Comparison with theoretical and experimental data available in the literature was carried out. These results should be consulted from the references [1,2]. Here, we will briefly show how we construct the TZ, TZP, ATZP, TZP-DKH, and ATZP-DKH basis set. For more informations, see refs. [1-7].

## Generation of the basis sets for Fr–Lr

A similar systematic to the one used before for the elements H–La and Hf–Rn [3-6] was applied to develop the TZ set. First, the exponents of the uncontracted sets were generated using the improved generator coordinate Hartree-Fock method [8]. Next, another subroutine, that optimizes all exponents of the uncontracted basis set, was used to improve the total HF energy of Fr–Lr. The ground-states of Fr (<sup>2</sup>S), Ra (<sup>1</sup>S), Ac (<sup>2</sup>D), Th (<sup>3</sup>F), Pa (<sup>4</sup>K), U (<sup>5</sup>L), Np (<sup>6</sup>L), Pu (<sup>7</sup>F), Am (<sup>8</sup>S), Cm (<sup>9</sup>D), Bk (<sup>6</sup>H), Cf (<sup>5</sup>I), Es (<sup>4</sup>I), Fm (<sup>3</sup>H), Md (<sup>2</sup>F), No (<sup>1</sup>S) and Lr (<sup>2</sup>P) and the ATOMSCF program [9] were used to carry out these optimization process. Finally, employing another subroutine developed by our research group and coupled to the ATOMSCF program, the best segmented contraction schemes were found: (22s15p10d4f)/[10s6p3d1f] for Fr and Ra, (22s15p13d4f)/[10s6p6d1f] for Ac [2], (22s15p13d7f)/[10s6p6d4f] for Th and Lr and (22s15p14d7f)/[10s6p7d4f] for Pa–No [2].

Table 1 displays the total HF energies for Fr–Lr calculated with the uncontracted and contracted TZ basis sets and with a numerical HF method [10]. As expected. The largest errors obtained with the uncontracted and contracted sets do not exceed 0.6 and 33.7 hartree, respectively.

To generate the TZP basis set, 2d1f (for Fr and Ra), 2f1g (for Ac) [1] and 2g (for Th–Lr) [2] polarization functions were added to the TZ set and, then, they were optimized using the ROMP2 perturbation theory and a subroutine coupled to the Gaussian 09 code [11]. At the end of this process the TZP basis has the form: [10s7p5d2f] for Fr and Ra, [10s6p6d3f1g] for Ac [1], [10s6p6d4f2g] for Th and Lr, and [10s6p7d4f2g] for Pa–No [2].

To have a good description of the electrons far from the nuclei, it is necessary to add to the TZP set diffuse functions. 1s1p1f (for Fr and Ra), 1s1p1d (for Ac) [1] and g (for Th–Lr) [2] functions were added to TZP sets and, then, optimized using the ground state total HF energies of the anions. This set was nominated ATZP. The ATZP basis set has the final forms: [11s8p6d3f] for Fr and Ra, [11s7p7d4f2g] for Ac, [11s7p7d5f3g] [1] for Th and Lr and [11s7p8d5f3g] for Pa–No [2].

**Table 1.** Ground state total HF energies (in hartree) for Fr–Lr.

Atom	Uncontracted set	TZ set	NHF <sup>a</sup>
Fr	-22474.98186 <sup>b</sup>	-22465.05278 <sup>b</sup>	-22475.85871
Ra	-23093.42671 <sup>b</sup>	-23082.67675 <sup>b</sup>	-23094.30367
Ac	-23721.34847 <sup>b</sup>	-23709.28275 <sup>b</sup>	-23722.19206
Th	-24359.09828	-24346.02588	-24359.62244
Pa	-25006.97962	-25006.95230	-25007.10987
U	-25664.22503	-25658.32465	-25664.33827
Np	-26331.32855	-26325.66044	-26331.45496
Pu	-27008.29096	-26998.00702	-27008.71944
Am	-27695.37525	-27685.07157	-27695.88722
Cm	-28392.48803	-28386.05559	-28392.77117
Bk	-29099.56557	-29092.49147	-29099.83161
Cf	-29817.04843	-29808.96591	-29817.41892
Es	-30544.58895	-30536.27693	-30544.97219
Fm	-31282.36641	-31274.99289	-31282.77760
Md	-32030.40099	-32022.05006	-32030.93297
No	-32789.07332	-32779.96213	-32789.51214
Lr	-33557.45934	-33524.26396	-33557.95041

<sup>a</sup>Numerical HF energy from Ref. [10].

<sup>b</sup>HF energy from Ref. [1].

We developed in the past DKH basis sets [5-7] for H–La and Hf–Rn from the non-relativistic ones [3,4,6,7], using the de Jong's et al. Procedure [12]. With the objective to include the scalar relativistic effects, the TZP basis set contraction coefficients for H–La and Hf–Rn [3-6] were recontracted with the DKH2 level and a subroutine developed by us and coupled into the Gaussian 09 code [11]. This set was nominated TZP-DKH. Throughout the process, the original exponents and contraction schemes are not altered.

Adding the diffuse functions generated for the TZP sets to the TZP-DKH sets for Fr–Lr, we obtain the basis sets designed as ATZP-DKH. The only difference between the ATZP and ATZP-DKH basis set is the contraction coefficients.

## Conclusions

For H–La and Hf–Rn, compact non-relativistic (TZP and ATZP) and relativistic (TZP-DKH and ATZP-DKH) segmented all-electron basis sets were generated by our research group [1-7]. The specific conclusions obtained from Fr–Lr should be consulted in the refs. [1,2].

We have shown that it is possible to develop all-electron segmented basis sets that have a good balance between accuracy and computational cost on atomic and molecular property calculations [1-7].

The XZP, AXZP, XZP-DKH, and AXZP-DKH (X = D (for the atoms from H to Lr), T (for the atoms from H to Ac and Th to Lr), Q (for the atoms from H to Xe), 5 and 6 (for the atoms from H to

Ar)) basis sets are available for download on different formats at <http://http://qcgv.ufes.br> and <https://bse.pnl.gov/bse/portal>

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