

## Segmented all-electron Gaussian basis sets of double and triple zeta qualities for Fr, Ra, and Ac

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**Introduction:** Segmented all-electron basis sets of valence double and triple zeta qualities plus polarization functions for the elements Fr, Ra, and Ac are generated<sup>1</sup> using non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonians. The sets are augmented with diffuse functions with the purpose to describe appropriately the electrons far from the nuclei. At the DKH-B3LYP level, first atomic ionization energies and bond lengths, dissociation energies, and polarizabilities of a sample of diatomics are calculated. Comparison with theoretical and experimental data available in the literature is carried out. It is verified that despite the small sizes of the basis sets, they are yet reliable. Here, we will discuss only the first ionization energies.

**Methods:** The Hartree-Fock (HF) and restricted openshell M $\phi$ ller-Plesset perturbation theory (ROMP2) methods were used to construct the nonrelativistic DZP and TZP basis set. The relativistic set was obtained from the DZP and TZP set by re-optimizing the values of the contraction coefficients using the second-order DKH Hamiltonian. At the end of this process, one obtains: DZP – [9s7p4d1f] for Fr and Ra and [9s6p5d2f] for Ac; TZP – [10s7p5d2f] for Fr and Ra and [10s6p6d3f1g] for Ac. It should be mentioned here that for Ac, it is not possible to optimize any function associated with the 7p orbital.

**Results and Discussion:** In Table 1 experimental and theoretical ionization energies for Fr, Ra, and Ac are displayed. For comparison, experimental<sup>2</sup> and other theoretical results<sup>3</sup> are also included. In general, the TZP-DKH results are in better accordance with the benchmark theoretical values<sup>3,4</sup> evaluated with the DK2-CASPT2/ANO procedure (without SO) than the DZP-DKH ones. The differences between the DKH2-B3LYP/TZP-DKH and DK2- CASPT2/ANO results do not exceed 0.131 eV, being the largest one for Ra. Pantazis and Neese<sup>5</sup> reported a value of 5.18 eV for Ac using the DKH2-B3LYP/[21s13p10d7f] model. The TZPDKH and ANO ionization energies for Fr and Ra agree well with the experimental values<sup>2</sup>, whereas for Ac, they are overestimate about 4.6%. For Ac, a 6d electron is removed in the ionization process, whereas for the other elements it is a 7s one. Considering the Ac element yet, one verified that the SO effects are not large<sup>4</sup> and that they get worse according to the experimental data<sup>2</sup>. So, the origin



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of the problem was attributed to the used electron correlation treatment. The expectancy for Fr and Ra is that the SO corrections be small since in both the cases an electron of s symmetry is ionized. Finally, it should be mentioned here that at the DKH2-B3LYP level of theory, the first ionization energies for Fr (4.154 eV) and for Ra (5.31 eV) calculated in this work with the large contracted ANO basis sets<sup>3,4</sup> are in good agreement with the TZP-DKH results.

	DZP-DKH <sup>a</sup>	TZP-DKH <sup>a</sup>	ANO basis set <sup>b</sup>	Expt. <sup>c</sup>
$Fr(^2S)$	3.869	4.024	3.929	3.942
Ra ( <sup>1</sup> S)	5.258	5.241	5.110	5.277
Ac $(^2D)$	5.350	5.231	5.21	5.00

Table 1. First ionization energies (in eV).

<sup>a</sup> Present investigation (DKH2-B3LYP calculations). Basis set generated in this work.

<sup>b</sup> DKH2-CASPT2 calculations (without SO)<sup>2,3</sup>. [12s11p8d5f] and (27s24p18d14f6g3h) basis sets for Fr and Ra and Ac, respectively.

<sup>c</sup> Experimental data from Ref. [2] averaged over the J quantum number.

**Conclusions:** Segmented basis sets (DZP, TZP, DZP-DKH, and TZP-DKH) for Fr, Ra, and Ac are developed to be employed in conjunction with the non-relativistic and DKH Hamiltonians. Theses sets are compact enough, but still accurate, to be competitive with the ECP valence basis sets. Computationally, they are more efficient than generally contracted basis sets on DFT calculations of large molecules and, according to our knowledge, the smallest all-electron basis set sizes of valence double and triple zeta valence qualities so far presented in the literature. The DKH2-B3LYP/TZP-DKH ionization energies are in excelente agreement with benchmark theoretical values<sup>3,4</sup>. Except for Ac, which is overestimate, they are close to the experimental data<sup>2</sup>. In summary, along these years 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. The XZP and XZP-DKH (X = D and T) basis sets for the atoms from H to Lr are available on different formats at http://qcgv.ufes.br.

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