



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

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Generation of the basis sets

Segmented all-electron basis sets of triple zeta valence qualities plus polarization functions for the elements Fr to Lr are generated 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, bond lengths and dissociation energies of a sample of diatomics are calculated for Fr, Ra and Ac. For the actinide monoxides, bond distances and dissociation energies are calculated with the B3LYP/ TZP-DKH procedure. 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.

Diffuse functions for Fr-Lr

In this work [1], a similar methodology presented in Ref. [2] is used, namely: 2d1f (for Fr and Ra), 2f1g (for Ac) and 2g (for Th-Lr) polarization functions are added to the TZ basis set, and these exponents were optimized for the restricted open-shell MP2 energy of the anion in the ground state. Next, functions s, p, d and f symmetries are added to the TZP basis sets generated for the neutral atoms and, then, optimized for the anion ground state HF energy.

The above calculations were carried out using the Gaussian 09 program. Throughout the calculations, we have employed spherical harmonic Gaussian-type functions.

This process conduces to the sets designed as ATZP – [11s8p6d3f] for Fr and Ra, [11s7p7d4f2g] for Ac, [11s7p7d5f3g] for Th and Lr and [11s7p8d5f3g] for Pa-No.

Computacional details

From the optimized DKH2-B3LYP/TZP-DKH bond lengths and dissociation energies computed. For the heavy atoms, the relativistic effects cannot be neglected. So, henceforth, only the relativistic basis sets in conjunction with the DKH2 Hamiltonian will be employed.

A selection of bond length and dissociation energy relativistic results for some diatomic are shown in Table 1. All theoretical values do not include the SO corrections. Experimental data is not available in the literature. For all dimers, the agreement between corresponding bond lengths obtained with the contracted and uncontracted sets is good. One can also note that there is a systematic reduction of the bond dissociation energies going from TZP- to ATZP-DKH. Lim et al. [3] using scalar relativistic pseudo potential (PP) coupled cluster and density functional along with the [9s9p8d5f3g] valence basis set obtained for Fr₂ dissociation energies that are in the range from 0.391 to 0.617 eV.

Here, we will discuss only the results for Fr-Ac. For Th-Lr, see reference [4]. For other atomic and molecular properties, see references [1, 4]

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Table 1: Theoretical bond lengths (r_e in Å) and dissociation energies (D_e in eV) for the ground states of some diatomics.

Molecule		ATZP-DKH ^a	Previous values
Fr ₂ (¹ Σ _g ⁺)	r_e	4.660	4.665 ^b 4.670 ^c
	D_e	0.546	0.409 ^b 0.446 ^c
Ra ₂ (¹ Σ _g ⁺)	r_e	5.460	5.478 ^b 5.478 ^c
	D_e	0.089	0.080 ^b 0.064 ^c
Ac ₂ (³ Σ _g ⁻)	r_e	3.700	3.635 ^b 2.163 ^c
	D_e	1.461	1.336 ^b 1.198 ^c
AcH (¹ Σ ⁺)	r_e	2.063	2.125 ^d 2.163 ^e
	D_e	3.670	3.63 ^d 3.58 ^e
AcO (² Σ ⁺)	r_e	1.967	1.930 ^d 2.023 ^e
	D_e	7.732	7.71 ^d 7.57 ^e
AcF (¹ Σ ⁺)	r_e	2.117	2.118 ^d 2.165 ^e
	D_e	7.638	7.65 ^d 7.38 ^e

^a Present investigation (DKH2-B3LYP calculation). All-electron basis set generated in Ref. [5] and in this work (sixth-row elements).

^b DKH2-CASPT2 calculations [6, 7]. All-electron ANO-[12s11p8d5f] and -[9s9p6d5f2g1h] basis sets for Fr and for Ra and Ac, respectively.

^c Present investigation (DKH2-B3LYP calculation). Uncontracted ATZP-DKH basis set generated in this work.

^d PP-CCSD(T) relativistic calculations [8]. Generally contracted [8s7p6d5f2g] valence basis set for Ac and aug-cc-pVQZ for H, O, and F.

^e DKH-BP86 calculations [9]. Large uncontracted all-electron universal Gaussian basis set for H, O, F, and Ac.

Conclusions

About the DKH2-B3LYP/ATZP-DKH bond lengths and dissociation energies reported in this work, one can say that in general they agree well with theoretical values calculated at a higher level of theory [CASPT2 and CCSD(T)].

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 TZP, ATZP, TZP-DKH, and ATZP-DKH basis sets for the atoms from H to Lr are available on different formats at <http://qcgv.ufes.br>.

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