



All-electron triple zeta basis sets for the actinides

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ARTICLE INFO

Keywords:

All-electron triple zeta basis sets

Segmented contraction

Actinides

DKH2-B3LYP calculations

Actinide monoxides

ABSTRACT

Non-relativistic and Douglas-Kroll-Hess (DKH) segmented all-electron basis sets of valence triple zeta quality plus polarization functions (TZP) for the actinides are developed. To describe accurately the properties that depend on a good description of the electrons far away from the nuclei, the corresponding augmented sets (ATZP and ATZP-DKH) are reported as well. For the actinide monoxides, bond distances, dissociation energies, natural charges and populations of the valence orbitals of the actinides, and bond indices are calculated with the B3LYP/TZP-DKH procedure. For Am and No, the B3LYP/ATZP-DKH static mean dipole polarizabilities are also computed. To assess the performance of these small size all-electron basis sets, comparison with theoretical and experimental data reported previously in the literature is done. These sets must be also helpful on calculations of properties involving simultaneously core and valence electrons.

1. Introduction

Among the actinide elements, only Th, U, and Pu are found in the nature, whereas Pa is produced from radioactive decay of uranium and Np, Am, Cm, Bk, and Cf are formed from transmutation reactions [1]. In contrast, the heavier actinides are formed when lighter elements are bombarded by neutrons. Some of the main applications of the early actinides are in the production of electrical energy and as catalysts in chemical reactions.

Due to the various difficulties (radioactivity, toxicity, and instability) that arises studying actinide compounds in laboratory, theoretical models become a promising alternative to understand the chemistry of the actinides. Consequently, the number of theoretical works about actinides has increased considerably in the last ten years (see, e.g., Refs. [2–12] and references therein). However, the quantity of complications that appear in a theoretical treatment of an actinide compound is not so different of that to carry out an experimental measure. Now, differently of the lanthanides, as the 5*f* orbital energy of the actinides is close to those of the 6*p*, 6*d*, and 7*s* orbitals, the amount of accessible oxidation states augments [13–15]. Besides, the relativistic effects as well as the electron correlation corrections are paramount [16] and they must be included in the calculations. To surpass these difficult many theoretical approaches were purposed. Among them, we can cite the effective core potential (ECP) [17], which is known to reduce the computational time of the calculations because only the

valence electrons are taken into account. Certainly, this approach is limited to evaluate properties that do not involve core electrons like EPR, Mössbauer and X-ray absorption spectra, and electron density analysis. An alternative to overcome these limitations is to use the density functional theory (DFT) along with a compact all-electron basis set coupled to the Douglas-Kroll-Hess (DKH) [18–20] Hamiltonian or to zeroth order regular approximation (ZORA) [21–23].

Differently from what happens for the light elements, the number of all-electron basis sets for the actinides found in the literature is significantly smaller. It is worth mentioning the ZORA basis sets of Slater-type functions (STFs) and the relativistic contracted basis sets available in the ADF [24] and PRIRODA-04 codes [25], respectively. The atomic natural orbital (ANO) basis sets [26] suitable for DKH-CASPT2 calculations. We must also cite the hierarchical sequences of correlation consistent basis sets developed by Peterson et al. [7,27] and by Dyall [28] to be used with the DKH and Dirac-Hartree-Fock Hamiltonians, respectively. The efficient use of the STFs is restricted to non-hybrid functional and to a limited number of codes, while the generally contracted ANO basis sets are appropriate for accurate *ab initio* calculations of small molecules. The computational efficiency of the generally contracted basis sets are significantly reduced when they are used in electronic structure codes written for segmented contracted sets. On the other hand, a general contracted basis set program can handle a segmented set without any loss of efficiency, because the latter set is a special case of the first one. For medium and large size molecules,

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where the use of integral screening becomes very important to reduce the computational cost of the calculations, the screening works more efficiently for segmented than for generally contracted basis sets [29]. Segmented all-electron relativistically contracted (SARC) basis sets for the actinides to be used with the second-order DKH (DKH2) and ZORA Hamiltonians were constructed by Pantazis and Neese [30]. The uncontracted (29s20p16d12f) and contracted [21s13p10d7f] SARC basis sets contain 253 and 159 functions, respectively.

Non-relativistic and relativistic segmented all-electron basis sets of valence triple zeta quality plus polarization functions (TZP) and the corresponding augmented sets (ATZP) for the elements from H to La and from Hf to Ac were generated by Jorge et al. [31–39]. These sets are compact enough to have a good balance between computational cost and accuracy and, consequently, they have been used with success on property calculations of atoms, molecules, and clusters [40–43]. Thus, the main objective of this article is to extend the TZP, ATZP, TZP-DKH, and ATZP-DKH basis sets for the elements from Th to Lr. For the actinide monoxides (AnO), bond lengths, dissociation energies, natural charges and populations of the valence orbitals of the actinides, and bond indices are calculated at the DKH2-DFT/TZP-DKH level of theory. In addition, ATZP-DKH mean dipole polarizabilities of Am and No are reported. Comparison with theoretical and experimental data published previously in the literature is carried out.

2. TZ, TZP, ATZP, TZP-DKH, and ATZP-DKH basis set generations

2.1. TZ basis set for Th-Lr

The used procedure in this work to construct the TZ basis set for the actinides is similar to that for the elements from Hf to Ac [37,38], namely: Firstly, a subroutine containing the improved generator coordinate Hartree-Fock (HF) method [44] is employed to generate the uncontracted basis set of each element. Next, another subroutine, that optimizes all exponents of the uncontracted basis set, is used to improve the total HF energy of Th-Lr. To carry out these optimization processes, the ground states of Th ($6d^27s^2$, 3F), Pa ($5f^26d^17s^2$, 4K), U ($5f^36d^17s^2$, 5L), Np ($5f^46d^17s^2$, 6L), Pu ($5f^67s^2$, 7F), Am ($5f^77s^2$, 8S), Cm ($5f^86d^17s^2$, 9D), Bk ($5f^97s^2$, 6H), Cf ($5f^{10}7s^2$, 5I), Es ($5f^{11}7s^2$, 4I), Fm ($5f^{12}7s^2$, 3H), Md ($5f^{13}7s^2$, 2F), No ($5f^{14}7s^2$, 1S), and Lr ($5f^{14}7s^27p^1$, 2P) and the ATOM-SCF code [45] are used. After some tests, we verify that it is necessary to add one more diffuse Gaussian function to describe correctly the $6d$ orbitals of the elements from Pa to No. In the optimization processes of these functions, the elements from Pa to No, whose $6d$ orbitals are not occupied in the ground state, an excited state arising from electronic configuration $5f^{n-1}6d^17s^2$ ($5f^{14}6d^17s^2$ for Lr) is taken into account. It should be mentioned here that for Th, the smallest Gaussian function exponents of f symmetry are optimized considering the $5f^16d^17s^2$ electronic configuration. From Pa through No, an excited state arising from electronic configuration $5f^{n-1}7s^27p^1$ ($6d^17s^27p^1$ for Th) is used to optimize the most diffuse function of the p symmetry. The HF method is employed to generate all these functions. At the end of all these processes the numbers of primitive Gaussian functions of the uncontracted basis set for the elements Th and Lr (22s15p13d7f) and for Pa-No (22s15p14d7f) are 181 and 186, respectively. Finally, a subroutine developed by our research group and coupled to the ATOM-SCF program is employed to find the best segmented contraction scheme for each atom. For that, the criterion of the smallest difference between the energies obtained with the uncontracted and contracted basis sets of each element is used. The contraction schemes as well as the TZ set for Th and Lr [10s6p6d4f] and for Pa-No [10s6p7d4f] can be found in the webpage <http://qcgv.ufes.br/>.

2.2. TZP basis set for Th-Lr

To generate the TZP basis set for the actinides, 2g polarization functions are added to the TZ set and, then, they are optimized using

the restricted open-shell second-order Møller-Plesset (ROMP2) perturbation theory and a subroutine coupled to the Gaussian 09 code [46]. This program is also used in the molecular calculations. In the ROMP2 calculations, the frozen core approximation and spherical Gaussian functions are employed. The number of correlated electrons in the ROMP2 calculations of each element is given in parenthesis: Th (4), Pa (5), U (6), Np (7), Pu (8), Am (9), Cm (10), Bk (11), Cf (12), Es (13), Fm (14), Md (15), No (16), and Lr (17). The TZP basis sets for Th and Lr [10s6p6d4f2g] and for Pa-No [10s6p7d4f2g] have 104 and 109 functions, respectively.

2.3. ATZP basis set for Th-Lr

To have a good description of the electrons far from the nuclei, it is necessary to add to the TZP set diffuse functions. These functions are indispensable on calculations of electron affinity, polarizabilities, optical rotation, and electronic circular dichroism. With this in mind, diffuse functions of s , p , d , and f symmetries are added to the TZP basis sets and, then, they are optimized considering the anion ground state HF energies. Next, the ROMP2 minimum energy criterion is applied to the ground states of the anions to choose the g diffuse functions to be added to the latter set. Consequently, the augmented TZP (ATZP) basis set for the actinides constructed in this work has the following final forms: [11s7p7d5f3g] for Th and Lr and [11s7p8d5f3g] for Pa-No.

2.4. TZP-DKH and ATZP-DKH basis sets for Th-Lr

For molecules containing heavy elements, the relativistic effects are significant, so, they must be taken into account on calculations of any chemical or physical property. A method widely used to estimate the scalar relativistic effects of atomic and molecular systems is the DKH [18–20]. De Jong et al. [47] verified that if the contraction coefficients of the cc-pVXZ ($X = D, T, Q, \text{ and } 5$) basis sets of the elements H, He, B–Ne, Al–Ar, and Ga–Br were re-optimized with the DKH Hamiltonian, undesirable results of some compounds could be avoided. So, with the objective to include the scalar relativistic effects, the TZP basis set contraction coefficients for H-La and Hf-Ac [31–33,37,38] were re-contracted at the DKH level. This set was nominated TZP-DKH [37–39].

For the actinides, the DKH2 Hamiltonian [48] and the Gaussian 09 code [46] are employed to reoptimize the contraction coefficients of TZP. It should be mentioned here that the exponents and contraction schemes of the non-relativistic basis set are not altered in this procedure. Even so, the radial changes of the wave function caused by core orbital contractions and valence orbital expansions are included. For the elements from Th to Lr, Brummelhuis et al. [49] showed that the DKH2 Hamiltonian is variational.

A similar process was employed by Pantazis and Neese [30] to develop relativistic basis sets for the actinides. Initially, ROHF calculations along with the series $\alpha_i \chi^{-i}$ ($i = 1, 2, 3, \dots$ and $\chi = 2.20, 2.40, 2.50, \text{ and } 2.60$ for $l = s, p, d, \text{ and } f$) were used to construct the uncontracted basis set. Then, the DKH2 and ZORA Hamiltonians were employed to determine the contraction coefficients of the SARC basis sets.

The ATZP-DKH basis set for the actinides is obtained adding the diffuse functions reported in Section 2.3 to the TZP-DKH set. It should be emphasized that the only difference between the ATZP and ATZP-DKH basis set is the contraction coefficients.

3. Results and discussion

As previously stated, to handle theoretically compounds containing actinides relativistic effects become essentials. Therefore, only the relativistic basis sets generated in this work (TZP-DKH and ATZP-DKH) in conjunction with the DKH2 Hamiltonian will be used henceforth.

The success of the B3LYP functional [50,51] on atomic and molecular property calculations is well known to all. This functional has

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