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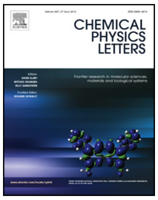

All-electron double zeta basis sets for the lanthanides: Application in atomic and molecular property calculations

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ABSTRACT

Segmented all-electron basis sets of valence double zeta quality plus polarization functions (DZP) for the elements from Ce to Lu are generated to be used with the non-relativistic and Douglas–Kroll–Hess (DKH) Hamiltonians. At the B3LYP level, the DZP-DKH atomic ionization energies and equilibrium bond lengths and atomization energies of the lanthanide trifluorides are evaluated and compared with benchmark theoretical and experimental data reported in the literature. In general, this compact size set shows to have a regular, efficient, and reliable performance. It can be particularly useful in molecular property calculations that require explicit treatment of the core electrons.

1. Introduction

Lanthanide complexes have been extensively used in catalysis and advanced materials [1,2]. Because their unique chemical and physical properties, the lanthanides have been applied with success in various areas, namely: molecular magnetism, biomedical field, fabrication of lasers, plasma displays, special glasses, etc. [3,4].

The difficulties in applying quantum chemical methods to the lanthanides are well known [5]. The large numbers of orbitals and electrons and both the relativistic and correlation effects must be simultaneously considered in the computational treatment of systems containing these elements. Several approaches to overcome these complications have been employed: semiempirical methods, density functional theory (DFT), and effective core potentials (ECPs), which treat only the valence electrons. Relativistic ECPs can provide reliable approximations to all-electron calculations of molecules containing heavy atoms when geometries and relative energies are involved [6–10].

However, for the lanthanides, the definition of valence electrons is not clear, consequently, there are principally three types of ECPs and related valence basis sets available [6–10]. Deficiencies of ECP have been highlighted in particular circumstances [11–13] as well as evident limitations arise when proprieties related to inner-shells are investigated, as in electron paramagnetic resonance, Mössbauer and X-ray absorption spectra, and electron density topological analysis. At least for such cases, it is indispensable to have appropriate all-electron basis sets to carry out calculations using popular scalar relativistic Hamiltonians, such as the Douglas–Kroll–Hess (DKH) [14–16] approach.

For Ce–Lu, some all-electron basis sets were reported in the literature: The scalar relativistic ZORA (zeroth order regular approximation) set of Slater-type functions available in the Amsterdam density functional program [17], the atomic natural orbital (ANO-RCC) basis sets of Roos et al. [18] generated from second-order DKH Hamiltonian (DKH2), the third-order DKH (DKH3) sets of Nakajima et al. [19,20], and the relativistic segmented basis sets of Sekiya et al. [21]. These three hierarchical sequences of high-quality basis sets of Gaussian-type-functions are appropriate to be used in calculations of small molecules. The general contraction was employed in the generation of the Roos and Nakajima basis sets, then, they become less efficient in DFT calculations, where the computational cost is strictly related to the number of two-electron integrals. Another point to be mentioned here is the low efficiency of quantum chemistry codes that do not take benefit of the general contraction. Segmented all-electron relativistically contracted (SARC) basis sets of valence triple zeta quality to be used with the DFT-DKH2 or -ZORA methods are developed by Pantazis and Neese [22]. The final uncontracted (23s16p12d6f) and contracted [18s12p9d3f] SARC basis sets have 173 and 120 functions, respectively. In 2011, Dolg [23] presented segmented contracted all-electron basis set (23s16p12d6f)/[18s12p9d3f] for La–Lu to be used at the DFT-DKH2 level of theory. It should be noted that these sets have similar sizes of those reported in Ref. [22]. However, these basis sets are still considered large to be employed in calculations

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of moderate size molecules containing lanthanides. Then, we feel the necessity to have more compact segmented all-electron basis sets, but yet reliable, to be used in scalar relativistic calculations of lanthanides.

In this work, we construct segmented all-electron basis sets of valence double zeta quality plus polarization functions (DZP) for the elements Ce–Lu to be used with the non-relativistic and DKH Hamiltonians. It should be noted that for the elements from H to Hf and from Ta to Rn, similar quality basis sets were previously published [24–29]. From the DZP-DKH basis set, DFT atomic ionization energies and equilibrium bond lengths and atomization energies of the lanthanide trifluorides are calculated and compared with benchmark theoretical and experimental data.

2. Determination of the basis sets

2.1. Valence double zeta basis set for Ce–Lu

For the lanthanides, a similar procedure to that used to develop the DZ set for Hf–Hg [29] is employed. After the valence space (4f5p5d6s) for these elements to be chosen, the uncontracted basis set of each atom is optimized considering the minimum ground-state [Ce (^{1}G), Pr (^{4}I), Nd (^{5}I), Pm (^{6}H), Sm (^{7}F), Eu (^{8}S), Gd (^{9}D), Tb (^{6}H), Dy (^{5}I), Ho (^{4}I), Er (^{3}H), Tm (^{2}F), Yb (^{1}S), and Lu (^{2}D)] total Hartree–Fock (HF) energy criterion. In this process, the improved generator coordinate HF method [30] is used. Next, with the purpose to improve the previous HF energy of each element, all exponents of the s, p, d, and f symmetries are optimized using a subroutine developed by our research group and that was incorporated to the ATOM-SCF program [31]. This program uses the restricted open-shell (RO) SCF procedure.

At the end of the HF optimization process, diffuse exponents ($\sim$0.18) of d symmetry for Ce and Lu had been generated, whereas for the other elements the same did not occur. With the purpose to describe a possible occupation of the 5d valence orbital when a chemical bond occurs, one more d function is added to the latter atoms and, then, optimized at the HF level. The exponents of these functions converged to $\sim$0.50.

Next, after carrying out hundreds of tests with the optimized uncontracted basis sets, the best segmented contraction scheme (smallest loss of HF energy) for each atom is found.

In Table 1, the total HF energies for Ce–Lu evaluated in this work with the uncontracted [(20s14p9d5f) for Ce and Lu and (20s14p10d5f) for Pr–Yb] and DZ basis sets are displayed. The numerical HF results [32] are also included. One can observe that the errors obtained with the uncontracted and DZ sets in general increase from Ce to Lu and that the largest ones occur for Yb (0.27869 and 22.97217 Hartree, respectively).

Table 1
Ground state total HF energies in Hartree (sign reversed) for Ce–Lu.

Atom	Uncontracted set	DZ set	NHF[a]
Ce (^{1}G)	8566.248622	8560.217932	8566.872681
Pr (^{4}I)	8921.007734	8909.244729	8921.181028
Nd (^{5}I)	9283.795665	9268.134876	9283.882944
Pm (^{6}H)	9654.995494	9639.094619	9655.098969
Sm (^{7}F)	10 034.83713	10 025.24412	10 034.95255
Eu (^{8}S)	10 423.41378	10 413.80094	10 423.54302
Gd (^{9}D)	10 820.46203	10 803.42812	10 820.66121
Tb (^{6}H)	11 226.39471	11 208.57945	11 226.56837
Dy (^{5}I)	11 641.26172	11 622.67160	11 641.45260
Ho (^{4}I)	12 065.06950	12 045.47532	12 065.28980
Er (^{3}H)	12 497.91571	12 477.89123	12 498.15278
Tm (^{2}F)	12 939.91177	12 919.27883	12 940.17440
Yb (^{1}S)	13 391.17750	13 368.48402	13 391.45619
Lu (^{2}D)	13 851.42601	13 829.67338	13 851.80800

[a] Numerical HF energy from Ref. [32].

2.2. Polarization functions for Ce–Lu

The non-relativistic DZP basis set is obtained from the DZ representation adding angular quantum number functions higher than those necessary to describe the ground-state atom. So, for the elements from Ce to Lu a function of g symmetry is added and, then, optimized using the minimum RO second-order Mϕller-Plesset perturbation theory (MP2) energy criterion. The frozen core approximation for electron correlation as available in the GAUSSIAN 09 program [33] is used. Throughout the calculations, spherical harmonic Gaussian-type functions are employed.

The resultant contracted DZP basis set is: [8s5p4d2f1g] (66 functions) for Ce and Lu and [8s5p5d2f1g] (71 functions) for Pr to Yb. It should be mentioned here that the small core ECP contracted valence basis set [10s8p5d4f] of Cao and Dolg has 87 functions [9].

2.3. Douglas–Kroll–Hess basis set for Ce–Lu

The scalar relativistic correction can be substantial, even for molecules that contain first-row elements (see Ref. [34]). The DKH approach [14–16] has been successfully used to estimate such scalar relativistic effects. To avoid undesirable results in relativistic calculations, the cc-pVXZ (X = D, T, Q, and 5) non-relativistic basis sets for H, He, B–Ne, Al–Ar, and Ga–Br are contracted again at the DKH level of theory by de Jong et al. [34]. In order to incorporate systematically the scalar relativistic effects, the DZP [24,25,27–29] basis set for H–La and Hf–Rn was also recontracted using the DKH Hamiltonian. This set was designated as DZP-DKH [26–29].

The DKH2 [35] Hamiltonian as implemented in the GAUSSIAN 09 program [33] is used to re-optimize the contraction coefficients of the DZP basis set for the elements from Ce to Lu, whereas the exponents and contraction schemes of the original set were not modified. In this process, a subroutine developed by our research group and coupled to the GAUSSIAN 09 to minimize the ground-state atom energy is used. The variational stability of the DKH2 Hamiltonian for all elements of the Periodic Table was proved by Brummelhuis et al. [36]. At the end of this procedure, one can say that the wave function radial changes due to relativistic contraction and expansion of the core and valence orbitals, respectively, are incorporated in the DZP-DKH basis set for Ce–Lu.

3. Results and discussion

For the lanthanides, it is essential to take into account relativistic effects in atomic and molecular calculations. In this Section, only the DZP-DKH basis set with the DKH2 Hamiltonian is used. Now, the spin-orbit (SO) coupling effect can be so large that to remove the atomic experimental fine-structure splittings from the experimental atomization energy is not enough. Atomic and molecular second-order SO couplings should also be considered. As these relativistic effects cannot be computed with the GAUSSIAN 09 code using an all-electron basis set, they are omitted.

Throughout the calculations, the B3LYP functional [37,38] is employed. For the lanthanide trifluorides, the atomization energies are calculated from the DKH2-B3LYP/DZP-DKH optimized geometries. In the optimization process, planar and pyramidal geometries are investigated.

3.1. Atomic calculations

Initially, at the DKH2 HF level, the ground state total energies of the elements from Ce to Lu are computed with DZP-DKH basis set and, then, using the benchmark theoretical results [6] obtained with the uncontracted universal Gaussian basis set (UGBS, containing 304 functions per atom) of de Castro and Jorge [39], the mean