

Diffuse basis functions for small-core relativistic pseudopotential basis sets and static dipole polarizabilities of selected lanthanides La, Sm, Eu, Tm and Yb

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Abstract The compact sets of the diffuse functions are suggested for better description of the polarization properties of the lanthanide atoms using the small-core effective core potentials and the corresponding basis sets. The pd and 2pdfg augmentations with exponents 0.028 and 0.015 (p), 0.032 (d) and 0.05 (f,g) are recommended for all lanthanides. Scalar and tensor dipole polarizabilities calculated using the multireference averaged quadratic coupled cluster method agree well with the literature data.

Keywords Atomic lanthanides · Dipole polarizability · Interaction potential

Introduction

Recent experiments with cold and ultracold atoms have heightened interest in collision dynamics of heavy transition metal atoms and the lanthanides (see, e.g., [1–9]). Ab initio methods have already proved useful for calculating both long-range and global interaction potentials capable of

reproducing the collision dynamics of such atoms at temperatures near 1 K [6, 10–15]. Nevertheless, the ab initio description of heavy atoms, in particular, lanthanides (LN), necessitates further validation and improvement to provide the level of accuracy required by the experiment at 1 K and lower temperatures. At the same time, the atomic parameters that determine polarization properties (and, therefore, long-range interactions) of LN atoms, are not known well enough.

The accurate description of the polarization properties of the open-shell LN atoms is challenging because of their complex electronic structure. Degenerate non-relativistic $2S+1L$ state of an atom with the electronic spin S and orbital L angular momenta splits in the DC electric field into $L + 1$ components according to the absolute value of the projection M of the orbital momentum on the field axis. To the first approximation, the splitting is determined by the dipole polarizability anisotropy with respect to field direction that can be represented either by Cartesian $\alpha_{\parallel}(L,M)$, $\alpha_{\perp}(L,M)$ or spherical $\alpha_0(L)$, $\alpha_2(L)$ components [14, 16, 17]. The latter pair, known as scalar and tensor components, respectively, is especially useful for representing the whole set of anisotropic polarizabilities of the L multiplet. From the simple orbital considerations α_0 and α_2 in lanthanides (as well as in the majority of the transition metals) reveal different origins [12]. The small tensor part arises from the inner open $(n-1)d$ or $(n-2)f$ shells, whereas the large scalar part is mostly determined by the outer spherical ns^2 shell. It is the screening of inner shells that makes α_0 so dominant over α_2 . Suppression of the polarizability anisotropy predicted by this simple model has found confirmation in the experimental and theoretical works devoted to atomic polarizabilities and dispersion interactions (for lanthanides, see Refs. [7, 8, 10, 15, 18, 19]). The high level of the accuracy is, therefore, needed to

Dedicated to Professor Marek T. Krygowski on the occasion of his 70th birthday.

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reproduce a small tensor component or, equivalently, a small splitting of the atomic terms in the field. The other important prerequisites are extensive multireference correlation treatments and an inclusion in the basis sets of the diffuse functions that are able to reproduce the polarization of the electronic charge cloud.

The present contribution focuses mainly on the latter issue. We provide compact augmentations of the existing basis sets [20, 21] based on the small-core relativistic effective core pseudopotentials (ECP) [22], and show that they uniformly improve the dipole polarizabilities computed for selected LN atoms (for illustrative purpose, the atoms with relatively low orbital angular momenta $L \leq 3$, La(2D), Sm(7F), Eu(8S), Tm(2F), and Yb(1S), have been chosen). The proposed augmentation should be useful for ab initio calculation of the complexes and molecules containing lanthanide atoms. The computed polarizabilities contribute to validation of the existing theoretical values.

Ab initio calculations

All ab initio calculations were done with the MOLPRO suite of programs [23].

To describe explicitly the inner $4f$ shell of LN atoms, the energy-consistent small-core ECPs by Dolg et al. [22] (referred to as ECP28MWB in the MOLPRO Internal Library and in the Stuttgart University Pseudopotential webpage [24]) were used. They describe 28 electrons occupying the inner shells with the principal quantum numbers $n = 1-3$. The remaining electrons occupying $n = 4(s,p,d,f)$, $n = 5(s,p,d)$, and $n = 6(s)$ shells were treated explicitly using the atomic natural orbital (ANO) (14s13p10d8f6g/6s6p5d4f3g) [20] or segmented (SEG) (14s13p10d8f6g/10s8p5d4f3g) [21] Gaussian basis sets augmented by the primitive diffuse functions as described below.

Calculations were carried out in the C_{2v} symmetry group with z -axis set by placing an artificial void (dummy) center at the distance of 25 Å from an LN atom. In the complete active space multiconfigurational self consistent field (CASSCF) method, $k + 2$ electrons forming the $4f^k 6s^2$ configuration were distributed over the corresponding 8 orbitals. For the La atom with $5d^1 6s^2$ configuration, 3 electrons were distributed over the 9 orbitals representing $5d$, $6s$ and $6p$ shells.

The CASSCF wave functions were used as the reference for the multireference averaged quadratic coupled cluster (AQCC) calculations [25, 26]. Nine orbitals with $n = 4(s,p,d)$ were included in the core, $5s$ and $5p$ orbitals were kept doubly occupied, and $4f$ and $6s$ (for La atom, $5d$, $6s$, and $6p$) orbitals were active. Polarizabilities were determined using the finite-field approach as the second

derivative on the dipole field strength by numerical differentiation with the field increment 0.0005 a.u.

For open-shell atoms polarizabilities were computed for Σ , Π , and Δ values of the projection of orbital momentum on the field axis. Scalar and tensor components were obtained as [14, 16, 17]

$$\alpha_0 = \frac{1}{3}(\alpha_\Sigma + 2\alpha_A), \quad \alpha_2 = \frac{2}{3}(\alpha_A - \alpha_\Sigma) \quad (1)$$

for $L = 2$ (La(2D)) or

$$\alpha_0 = \alpha_A, \quad \alpha_2 = \frac{5}{4}(\alpha_A - \alpha_\Sigma) \quad (2)$$

for $L = 3$ (Sm(7F) and Tm(2F)). The difference in α_Π values computed directly and derived from α_0 , α_2 was taken as a probe of accuracy. It did not exceed few hundredths of atomic unit.

Polarizability of the closed-shell Yb atom was also calculated within the restricted version of the coupled cluster method with single, double, and non-iterative triple excitations, RCCSD(T) [27], with the same choice of core orbitals and RHF wave function as the reference.

As an additional criterion for selecting the exponents of diffuse functions, we used the interaction energy of the Yb–He complex calculated at the RCCSD(T) level of theory as described in Refs. [10, 28]. Since at the long range the latter is dominated by the dipole–dipole dispersion energy, the attraction of the Yb and He moieties may be used as a good indicator of the adequacy of the basis set in the polarizability and dispersion problems.

Results

The optimization of diffuse function exponents was carried out for Yb atom against a benchmark value. The benchmark polarizability value was found using the 3s3p3d3f3g set with the exponents taken roughly as the even-tempered continuations for two smallest exponents of ANO basis (the range of exponents were 0.01–0.0025 for s, 0.02–0.005 for p, and 0.05–0.0125 for d, f, g). Then the ANO basis was sequentially augmented, one function at a time, by p, pd, 2pd, 2pdf, 2pdfg, and s2pdfg sets and the exponent of an added function was optimized to give the best agreement with the benchmark polarizability value and the Yb–He interaction energy. This sequence reflects our previous analysis [10], where the pd augmentation was suggested and negligible role of the diffuse s functions was established. The exponents so obtained are 0.01 for s, 0.028 and 0.015 for p, 0.032 for d, and 0.05 for f and g. With these sets, the calculations were performed for other LN atoms.

The results are presented in Table 1. It is evident that the ANO basis greatly underestimates the polarizabilities and

Table 1 Polarizabilities of the lanthanide atoms, a.u. For open-shell atoms scalar and tensor components are given as α_0 ; α_2 . For Yb atom, RCCSD(T) values are given in parentheses

Basis	Augmentation	La(2D)	Sm(2F)	Eu(8S)	Tm($^2F^\circ$)	Yb(1S)
ANO		121.2; 6.7	103.3; -1.2	101.9	89.4; -1.5	88.1 (87.5)
SEG				101.4		87.5
ANO	p	200.0; 8.9	184.2; -1.2	179.6	147.7; -1.7	147.3 (146.2)
ANO	pd	214.8; 13.4	196.0; -1.7	189.1	152.4; -2.1	151.9 (152.9)
ANO	2pd	214.7; 13.4	196.0; -1.7	191.7	152.0; -2.2	151.4 (153.0)
ANO	2pdf	220.7; 14.1	198.2; -1.8	191.0	153.0; -2.3	152.5 (153.1)
ANO	2pdfg	221.1; 14.0	198.5; -1.8	191.0	153.3; -2.3	152.7 (153.1)
ANO	s2pdfg	220.0; 14.0	198.0; -1.8	192.0	153.1; -2.3	152.3
SEG	s2pdfg			190.7	153.0; -2.2	152.3
ANO	3s3p3d3f3g	219.8; 13.8	196.8; -1.8	189.7	152.2; -2.2	151.2
SEG	3s3p3d3f3g			189.4		151.0
Ref. ^a		209.9; 10.4 \pm 0.4	194.3; -3.5 \pm 0.2	186.9	147.1; -2.8 \pm 0.2	141.7
TDDFT ^b		200.9; 10.1	200.0; -5.0	194.3	161.4; -2.3	157.3

^a Scalar components from Ref. [29], tensor components from Refs. [18, 19, 30].

^b Ref. [15].

that the sequential augmentation obtained for Yb atom uniformly improves them bringing in close agreement with the ANO+3s3p3d3f3g values for all LN atoms considered. For the largest 2pdfg and s2pdfg sets, maximum deviation for α_0 does not exceed 1.0 and 1.2%, respectively, while the average error amounts to 0.7 and 0.6%. The benchmark values for the tensor component are reproduced for all LN atoms except for La, where the error approaches 1.4%. The necessary minimum pd augmentation provides the average accuracy of 0.7 and 6% for scalar and tensor components, respectively. Some tests performed with the segmented basis, that uses a different contraction of the same primitives as ANO, give very similar results.

Comparison with a limited set of literature data is possible. Theoretical values of scalar polarizabilities collected in the compilation of Miller [29], as well as the values of experimentally determined tensor polarizabilities from Refs. [18, 19, 30], are quoted as “Ref.”. Our results for scalar component are slightly above these values. The magnitude of the tensor component appears underestimated for the Tm and Sm atoms, but overestimated for the La atom. Recent time-dependent density functional calculations with self-interaction corrected potential (TDDFT) [15] give scalar polarizabilities in good agreement with our values, except for La. TDDFT tensor polarizabilities agree with the measurements somewhat better than the present ones. For Yb, α_0 was computed at different levels of ab initio theory by Wang and Dolg [31]. Their CCSD(T) value obtained with the previous version of ANO basis set massively augmented by diffuse functions, 145.3 a.u., is not far from the present results.

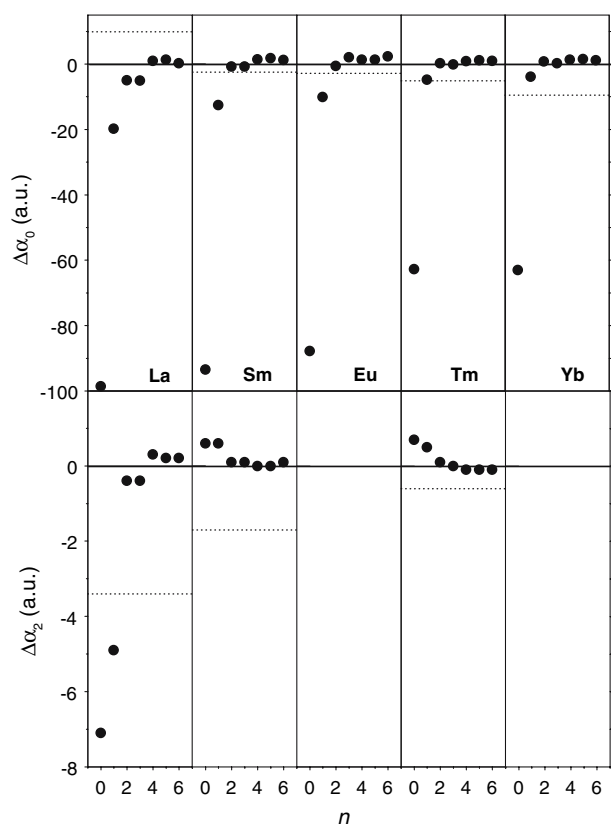


Fig. 1 Convergence of the calculated scalar (upper panel) and tensor (lower panel) polarizabilities for selected LN atoms. Absolute deviations from the benchmark ANO+3s3p3d3f3g results (taken as zero) are shown depending on n , the number of primitive functions in the ANO, ANO+p, +pd, +2pd, +2pdf, +2pdfg, +s2pdfg sequence. Dotted lines represent reference results cited in the text and Table 1.

It is instructive to analyze the incremental change of the polarizabilities upon the addition of the diffuse function with different angular momentum l . In Fig. 1, we plotted the absolute deviations from the ANO+3s3p3d3f3g values (taken as zero) as the function of the number of diffuse primitive functions in the consecutive p, pd, 2pd, 2pdf, 2pdfg, and s2pdfg augmentations with $n = 0$ corresponding to the bare ANO basis sets. For the scalar component, the huge gain always occurs upon addition of the single p-symmetry primitive ($n = 1$), much less pronounced effect is caused by the d-function ($n = 2$), the functions with higher angular momenta produce changes hardly visible on the scale of the figure, though for La atom with its open 5d-shell the effect of f-function is noticeable. In contrast, the tensor polarizability component is mostly sensitive to the d-function, while for La atom, both p- and f-functions are also important. These variations can be interpreted within the analysis by Sadlej [32], who proved that $l \pm 1$ functions are necessary to describe polarization of the shell with angular momentum l . It is also compatible with attributing the scalar polarizability component to the outer 6s shell and the tensor component to the inner 4f (or 5d) shell of LN atoms. The relatively small polarizability anisotropy is thus due to the screening of the high- l open-shell electrons by the external electrons occupying $l = 0$ orbital.

Augmented ANO basis sets should be useful for studying the weakly-bound interactions involving LN atoms. Our recent studies of the Yb_2 , TmYb dimers [28] and TmHe, YbHe complexes [10, 28] have already shown remarkable improvement of the interaction energies and dispersion coefficients. Being relatively compact, these bases can also be recommended for advanced computational studies of the more complex systems involving lanthanides, like various coordination compounds [33], and, in particular, fullerenes containing lanthanide ions that reveal interesting aromatic properties [34–36].

Conclusions

The relatively compact sets of the diffuse functions for augmenting the ANO basis sets for the small-core effective core potentials are suggested for lanthanide atoms. We found that the sets with the same exponents uniformly improve the description of atomic polarizabilities for selected LN atoms. The minimum pd augmentation allows one to reproduce the scalar polarizability within 1% accuracy, whereas 2pdfg set is recommended for more precise applications. Analysis of the incremental polarizability changes upon addition of functions with different angular momenta supports the shell model that attributes scalar polarizability to the external 6s shell and tensor polarizability to the open 4f (5d) shell.

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References

1. Stalnakier JE, Budker D, Freedman SJ, Guzman JS, Rochester SM, Yashchuk VV (2006) Phys Rev A 73:043416
2. Hancox CI, Doret SC, Hummon MT, Krems RV, Doyle JM (2005) Phys Rev Lett 94:013201
3. Honda K, Takasu Y, Kuwamoto T, Kumakura M, Takahashi Y, Yabuzaki T (2002) Phys Rev A 66:021401
4. Takasu Y, Honda K, Komori K, Kuwamoto T, Kumakura M, Takahashi Y, Yabuzaki T (2003) Phys Rev Lett 90:023003
5. Takasu Y, Maki K, Komori K, Takano T, Honda K, Kumakura M, Yabuzaki T, Takahashi Y (2003) Phys Rev Lett 91:040404
6. Krems RV, Kłos J, Rode MF, Szczyński MM, Chałasiński G, Dalgarno A (2005) Phys Rev Lett 94:013202
7. Hancox CI, Doret SC, Hummon MT, Luo L, Doyle JM (2004) Nature (London) 431:281
8. Krems RV, Buchachenko AA (2005) J Chem Phys 123:101101
9. McClelland JJ, Hanssen JL (2006) Phys Rev Lett 96:143005
10. Buchachenko AA, Szczyński MM, Chałasiński G (2006) J Chem Phys 124:114301
11. Kłos J (2005) J Chem Phys 123:024308
12. Kłos J, Rode MF, Rode JE, Chałasiński G, Szczyński MM (2004) Eur Phys J D 31:429
13. Buchachenko AA, Chałasiński G, Szczyński MM, Krems RV (2006) Phys Rev A 74:022705
14. Chu X, Groenenboom GC, Dalgarno A (2005) Phys Rev A 72:032703
15. Chu X, Dalgarno A, Groenenboom GC (2007) Phys Rev A 75:032723
16. Angel JRP, Sandars PGH (1968) Proc Roy Soc London A 305:125
17. Khadjavi A, Lurio A, Happer W (1968) Phys Rev 167:128
18. Rinkleff R-H, Thorn FZ (1968) Phys D 31:31
19. Rinkleff R-H, Thorn FZ (1994) Phys D 32:173
20. Cao X, Dolg M (2001) J Chem Phys 115:7348
21. Cao X, Dolg M (2002) J Mol Struct (THEOCHEM) 581:139
22. Dolg M, Stroll H, Preuss H (1989) J Chem Phys 90:1730
23. Werner H-J, Knowles PJ, with contribution from Amos RD, et al. computer code MOLPRO (2002)
24. <http://www.molpro.net>, <http://www.theochem.uni-stuttgart.de/pseudopotentials>
25. Szalay PG, Bartlett R (1993) J Chem Phys Lett 214:481
26. Szalay PG, Bartlett RJ (1995) J Chem Phys 103:3600
27. Knowles PJ, Hampel C, Werner H-J (1993) J Chem Phys 99:5219
28. Buchachenko AA, Chałasiński G, Szczyński MM (2007) Eur Phys J D 45:147
29. Miller TM (2002) In: CRC Handbook of Chemistry and Physics, 83rd edn. CRC Press, Boca Raton, FL, pp 10–163
30. Rinkleff R-H, Steudel A, Zieske KZ (1991) Phys D 18:101
31. Wang Y, Dolg M (1996) Theor Chem Acc 100:124
32. Sadlej AJ (1988) Collect Czech Chem Commun 53:1999
33. Edelman FT (2006) Coord Chem Rev 250:2511
34. Saito Y (1995) Carbon 33:979
35. Shinohara H (2000) Rep Prog Phys 63:843
36. Liu S, Sun SJ (2000) Organomet Chem 599:74