Gaussian Basis Sets for the Calculation of Some States of the Lanthanides

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Highly accurate adapted Gaussian basis sets are used to study the ground and some excited states for the neutral atoms and also some corresponding 6s and 4f ionized states from Cs through Lu. Our total energies are compared with those calculated with a numerical Hartree-Fock method. The mean error of our energy results is equal to 0.74 mhartree. Our calculations reproduce the experimental trend to increase or to decrease the 6s and 4f ionization potentials with increasing atomic number, although they are respectively smaller and larger than the experimental values.

I Introduction

In this last decade lanthanide chemistry and physics have experienced tremendous growth, for example in the field of catalysts [1] and high temperature superconductors [2]. Thus, it would be highly desirable to elucidate the electronic structure of lanthanide atoms at least in the Hartree-Fock (HF) approximation. For these atoms, numerical HF (NHF) calculations [3-5] were performed mainly on the ground states.

In this work, the adapted Gaussian basis sets [AGBSs - one different set of Gaussian-type function (GTF) exponents for each atomic species for the atoms from Cs (Z=55) through Lu (Z=71) [6] are initially augmented until saturation is achieved for each symmetry of each atom and then, using the generator coordinate HF (GCHF) [7] method, they are reoptimized for each atomic species. Next the energies for the atoms Cs-Lu and their positive ions are calculated and compared with those obtained with a NHF [5] method. The ionization potentials (IPs) are also computed and compared with the corresponding experimental values [8,9].

II The method

An approach to select the basis sets arises from the GCHF method [7]. In the GCHF method the one-electron functions are integral transforms, i.e.,

$$\Psi_1(1) = \int \phi_i(1,\alpha) f_i(\alpha) d\alpha \quad i = 1, ..., n, \tag{1}$$

where ϕ_i are the generator functions (GTFs in our case), f_i are the unknown weight functions, and α is the generator coordinate. The application of the variational principle to calculate the energy expectation value built with such one-electron functions leads to the Grifftn-Hill-Wheeler-HF (GHWHF) equations [7]. The GHWHF equations are integrated using a procedure known as integral discretization (ID) [10]. The ID technique is implemented through a relabelling of the generator coordinate space, i.e.,

$$\Omega = \ln \frac{\alpha}{A}, \quad A > 1 \tag{2}$$

where A is a numerically determined scaling factor. In the new generator coordinate space Ω, an equally spaced N-point mesh $\{\Omega_i\}$ is selected, and the integration range is characterized by a starting point $\Omega_{\min}$, an increment $\Delta\Omega$, and N (number of discretization points). The highest value ($\Omega_{\max}$) for the generator coordinate is given by

$$\Omega_{\max} = \Omega_{\min} + (N-1)\Delta\Omega \ . \tag{2}$$

The choice of the discretization points determines the exponents of the GTFs.

In the last four years, the GCHF [7] method was successfully tested in the generation of basis sets for atomic and molecular systems [11-16].

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III III Results and discussion

By employing the GCHF method we have generated AGBSs for the atomic species presented in Table 1. Throughout the calculations we have used the scaling factor A (see Eq. (2)) equal to 6.0, and for all atomic species we have sought the best discretization parameter ($\Omega_{\min}$ and $\Delta\Omega$) values for each s, p, d and f symmetries. All calculations were carried out using a modified version of the ATOMSCF program [17], and for each atomic species the optimization process is repeated until the total energy value is stabilized within ten significant figures. The resulting wave functions are available by request through the e-mail address jorge@cce.ufes.br.

Table I shows the ground and some excited state HF total energies (in hartrees) for the neutral atoms and some cations from Cs (Z=55) through Lu (Z=71) computed with our AGBSs and with a NHF [5] method. Our basis set sizes are presented in the seventh column. We recall that the AGBSs are generated from the basis sets of Ref. [6]. First, we augmented these basis sets until saturate each symmetry of each atom, and second, using the GCHF [7] method, we reoptimized each AGBS of each atomic species studied here. From Table I, we can see that our total energies, for all atomic specie of interest, are in good agreement with the corresponding NHF [5] values and that our energy errors do not exceed 1.72 mhartree. Here it is important to say that the vector coupling coefficients used in the calculations of the open-shell configurations have been taken from the tabulation by Malli and Olive [18]. These tables show the vector coupling coefficients for the electron configurations s, p^n, sp^n, d^n, sd^n, $\mathrm{p}^m\mathrm{d}^n$, $\mathrm{sp}^m\mathrm{d}^n$ and f^n. The HF total energies of the ground states of the atoms Ce and Gd and of some states of the cations Pr^+, Nd^+, Pm^+, Sm^+, Eu^+, Tb^+, Dy^+, Ho^+, Er^+ and Tm^+ are not calculated here, because the electron configurations of these atomic species have 5d and 4f and 6s and 4f open shells, respectively. The electron configuration of Lu^+ (^{3}H) has 5d and 4f open shells, and thus the wave function for this cation is not generated here.

Table II contains the IPs (in eV) computed by using the Koopmans theorem (ε is our orbital energy), the total energy difference $\Delta E = E(X^+) - E(X)[X$ is the atomic symbol and $E(X^+)$ and $E(X)$ are our total energies respectively for the cation and the neutral atom presented in Table I], and the experimental values ($E_{\text{expt.}}$) [8,9].

From Table II we can see that the differences between our IP's calculated through $-\varepsilon$ (see the fourth column) and through ΔE (see the fifth column) are small for 6s orbital, indicating that the Koopmans theorem works for the 6s ionization. Besides this, for the 6s orbitals, our IPs calculated with these two approaches are very similar to those computed with a NHF method (see the sixth column). For all lanthanide atoms presented in Table II, and from our results for $-\varepsilon$, we can see that the 6s orbitals are more diffuse than the corresponding 4f orbitals, that is, the 6s IPs are smaller than the 4f lPs. For these atoms, it is known that the mean values of r for the 6s orbitals are larger than those for the 4f orbitals, that is, the 6s electrons are far from the nucleus than the 4f electrons. From La through Eu, both the calculated $-\varepsilon$ (~4.4-4.6 eV) and the experimental (~5.4-5.8 eV) 6s IPs are almost constant. After Tb, the $-\varepsilon$ and experimental [8,9] IPs gradually increase. The experimental IPs are always larger than the $-\varepsilon$ values. To correct this discrepancy, it is necessary to include in the calculations electron correlation effects and relativistic corrections, but this is outside the scope of this work. Here, it is important to say that Jorge *et al.* have developed the generator coordinate Dirac-Fock (GCDF) [19,20] method for closed-shell atoms and a segmented contraction methodology for relativistic Gaussian basis sets [21,22]. From Table II, only Yb (Z=70) has closed-shell, thus, for the other atoms presented in this Table, we cannot use the GCDF method to calculate the relativistic IPs.

Besides this, Table II shows that for the lanthanides, the 4f IPs calculated by us through $-\varepsilon$ and through ΔE give very different results. The ionization of the electrons in the outermost 6s shell causes small reorganization on the whole electron distribution, whereas the inner 4f electron ionization causes larger reorganization effects because of the appearance of a hole in the inner shell. Thus, for these atoms, it is not appropriated to use the Koopmans theorem to calculate the 4f electron ionization. For all lanthanide atoms, the 4f IPs calculated by us (ΔE) are in good agreement with the corresponding values obtained with a NHF [5] method, and although the calculated 4f IPs are 1-3 eV greater than the corresponding experimental values [8,9], NHF and our ΔE calculations describe the experimental trend well.

IV Conclusions

In this work we have generated AGBSs for the 45 atomic species presented in Table I with the GCHF [7] method. The largest difference between the total energies calculated by us and by a NHF [5] method is equal to 1.72 mhartree for Lu. Although our 6s and 4f IPs ($-\varepsilon$ and ΔE) are respectively smaller and larger than the corresponding experimental values [8,9], our calculations reproduce the experimental trends on the 6s and 4f electron ionizations well. For the 4f IPs, our ΔE results are better than those computed with the Koopmans theorem, whereas for 6s IPs the two approaches give similar results.

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Table I. Ground and some excited state Hartree-Fock (HF) total energies (in hartree) for the neutral atoms and some cations from Cs through Lu.

						Present work[a]		
Z	Atom	6s	5p	5d	4f	AGBS sizes	E (AGBSs)	E (NHF)[b]
55	Cs$^+$ (^{3}P)	1	5	0	0	31s23p16d	-7553.300775	-7553.30109
55	Cs$^+$ (^{1}S)	0	6	0	0	31s23p16d	-7553.809897	-7553.81032
55	Cs (^{2}S)	1	6	0	0	31s23p16d	-7553.933158	-7553.93365
56	Ba$^+$ (^{2}P)	2	5	0	0	32s23p16d	-7882.699357	-7882.69970
56	Ba$^+$ (^{2}S)	1	6	0	0	32s23p16d	-7883.391878	-7882.39188
56	Ba (^{1}S)	2	6	0	0	32s23p16d	-7883.543396	-7883.54382
57	La$^+$ (^{3}F)	2	5	1	0	31s25p19d	-8220.120943	-8220.12136
57	La$^+$ (^{3}H)	0	6	0	2	31s25p19d11f	-8220.747938	-8220.74876
57	La$^+$ (^{1}S)	2	6	0	0	31s25p19d	-8220.831165	-8220.83156
57	La$^+$ (^{3}D)	1	6	1	0	31s25p19d	-8220.908234	-8220.90861
57	La (^{2}F)[c]	2	6	0	1	31s25p19d11f	-8221.063346	-8221.06381
57	La (^{2}D)	2	6	1	0	31s25p19d	-8221.066259	-8221.06670
58	Ce$^+$ (^{2}D)	2	6	1	0	32s22p16d11f	-8566.330093	-8566.33091
58	Ce$^+$ (^{2}F)	2	6	0	1	32s22p16d11f	-8566.611918	-8566.61237
58	Ce (^{3}H)[c]	2	6	0	2	32s22p16d11f	-8566.918882	-8566.91957
59	Pr$^+$ (^{3}H)	2	6	0	2	32s24p17d12f	-8920.819709	-8920.82088
59	Pr (^{4}I)	2	6	0	3	32s24p17d12f	-8921.180552	-8921.18102
60	Nd$^+$ (^{4}I)	2	6	0	3	31s24p17d13f	-9283.519394	-9283.51980
60	Nd (^{5}I)	2	6	0	4	31s24p17d13f	-9283.882339	-9283.88294
61	Pm$^+$ (^{5}I)	2	6	0	4	31s25p17d13f	-9654.735827	-9654.73624
61	Pm (^{6}H)	2	6	0	5	31s25p17d13f	-9655.098345	-9654.09896
62	Sm$^+$ (^{6}H)	2	6	0	5	31s23p16d12f	-10034.54262	-10034.5432
62	Sm (^{7}F)	2	6	0	6	31s23p16d12f	-10034.95178	-10034.9525
63	Eu$^+$ (^{7}F)	2	6	0	6	32s23p16d12f	-10423.06812	-10423.0687
63	Eu (^{8}S)	2	6	0	7	32s23p16d12f	-10423.54234	-10423.5430
64	Gd$^+$ (^{8}S)	2	6	0	7	31s24p17d13f	-10820.41271	-10820.4133
64	Gd (^{7}F)[c]	2	6	0	8	31s24p17d13f	-10820.61651	-10820.6173
65	Tb$^+$ (^{7}F)	2	6	0	8	32s24p16d12f	-11226.29073	-11226.2914
65	Tb (^{6}H)	2	6	0	9	32s24p16d12f	-11226.56769	-11226.5684
66	Dy$^+$ (^{6}H)	2	6	0	9	31s22p17d12f	-11641.12737	-11641.1283
66	Dy (^{5}I)	2	6	0	10	31s22p17d12f	-11641.45139	-11641.4526
67	Ho$^+$ (^{5}I)	2	6	0	10	31s22p17d12f	-12064.97708	-12064.9779
67	Ho (^{4}I)	2	6	0	11	31s22p17d12f	-12065.28855	-12065.2898
68	Er$^+$ (^{4}I)	2	6	0	11	32s23p16d12f	-12497.85416	-12497.8549
68	Er (^{3}H)	2	6	0	12	32s23p16d12f	-12498.15181	-12497.1528
69	Tm$^+$ (^{3}H)	2	6	0	12	32s23p15d12f	-12939.83107	-12939.8320
69	Tm (^{2}F)	2	6	0	13	32s23p15d12f	-12940.17326	-12940.1744
70	Yb$^+$ (^{2}P)	2	5	0	14	32s22p16d12f	-13390.33045	-13390.3314
70	Yb$^+$ (^{2}F)	2	6	0	13	32s22p16d12f	-13391.04533	-13391.0463
70	Yb$^+$ (^{2}S)	1	6	0	14	32s22p16d12f	-13391.27930	-13391.2803
70	Yb (^{1}S)	2	6	0	14	32s22p16d12f	-13391.45499	-13391.4562
71	Lu$^+$ (^{3}F)	2	5	1	14	31s23p18d12f	-13850.56605	-13850.5675
71	Lu$^+$ (^{3}D)	1	6	1	14	31s23p18d12f	-13851.62338	-13851.6249
71	Lu$^+$ (^{1}S)	2	6	0	14	31s23p18d12f	-13851.59948	-13851.6010
71	Lu (^{2}D)	2	6	1	14	31s23p18d12f	-13851.80628	-13851.8080

[a] HF total energies obtained with our adapted Gaussian basis sets (AGBSs).
[b] Numerical HF (NHF) total energies obtained from Ref. [5].
[c] Excited state in the neutral atom.

Table II. Ionizations potentials (in eV) for 6s and 4f electrons.

			Ionization Potentials (IPs)			
Z	Atom	Orbital	$-\varepsilon^a$	ΔE^b	ΔE^c	Expt.[d]
55	Cs (^{2}S)	6s	3.365	3.354	3.356	3.893
56	Ba (^{1}S)	6s	4.279	4.123	4.134	5.210
57	La (^{2}D)	6s	4.637	4.300	4.302	5.812
59	Pr (^{4}I)	6s	4.461	-	4.254	5.422
		4f	14.951	9.819	9.800	(7.40)
60	Nd (^{5}I)	6s	4.506	-	4.288	5.489
		4f	16.201	9.876	9.881	(7.66)
61	Pm (^{6}H)	6s	4.560	-	4.321	5.554
		4f	17.107	9.865	9.870	(7.66)
62	Sm (^{7}F)	6s	4.600	-	4.607	5.631
		4f	18.107	11.134	11.139	(8.61)
63	Eu (^{8}S)	6s	4.651	-	4.381	5.666
		4f	19.361	12.904	12.906	(9.76)
65	Tb (^{6}H)	6s	4.748	-	4.505	5.852
		4f	18.906	7.536	7.537	(6.53)
66	Dy (^{5}I)	6s	4.783	-	4.564	5.927
		4f	19.126	8.817	8.825	7.456
67	Ho (^{4}I)	6s	4.833	-	4.621	6.018
		4f	19.269	8.476	8.487	(7.26)
68	Er (^{3}H)	6s	4.874	-	4.678	6.101
		4f	19.340	8.099	8.105	(6.97)
69	Tm (^{2}F)	6s	4.918	-	4.732	6.184
		4f	19.552	9.311	9.318	7.728
70	Yb (^{1}S)	6s	4.958	4.781	4.785	6.254
		4f	19.909	11.147	11.153	8.910
71	Lu (^{2}D)	6s	5.405	4.977	4.981	6.888
		4f	29.299	-	19.455	(16.2)

[a] IPs calculated by using Koopmans theorem. ε is the orbital energy calculated by us.

[b] IPs calculated by using the difference between our cation and neutral atom total energies [$\Delta E = E(X^+) - E(X)$, X is the atomic symbol] given in Table I.

[c] IPs obtained with a numerical HF method [5].

[d] Experimental IPs for the 6s and 4f electrons are those given in Refs. [8,9]. The numbers in the parentheses are estimated ones (see Ref. [9]).