Neutral atoms and ion energies, accurate ionization potential, and electron affinities by polynomial generator coordinate Hartree–Fock method

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Abstract: We have developed accurate Gaussian basis functions obtained with the polynomial generator coordinate Hartree–Fock (p-GCHF) method for H, Zn, and Ga-Kr atoms. These basis sets have been applied in the calculation of nonrelativistic energies for neutral atoms, monovalent cations, monovalent anions, ionization potential (IP), and electron affinity (EA), with the objective of proving the quality of the basis set generated by the p-GCHF method. The total energies calculated for neutral atoms and monovalent cations and respective IP were minimally affected by the addition of polarization functions and their precision was comparable to the values reported in the literature. The relative errors were lower than 6.0×10^{-5} % and 7.0×10^{-5} % for neutral atoms and monovalent cations, respectively. The IP results were strictly equal to numerical Hartree–Fock (NHF) calculations and comparable to some experimental values. For monovalent anions, the nonrelativistic total energies were better than the Slater-type functions results and the relative errors were lower than 0.05% when compared to NHF. The EA results were the same as those obtained with NHF calculations reported in the literature for heavier elements. For IP and EA, our results followed the same periodic tendency when compared with experimental data.

Key words: Gaussian basis set, ionization potential, electron affinity, polarization functions

1. Introduction

Electronic structure calculations for atoms and molecules are usually carried out by the expansion of orbitals into a finite set of functions known as a basis set.[1] The use of Gaussian-type functions (GTFs) and Slater-type functions (STFs) is based on the method proposed by Roothaan.[2] From this point, two new perspectives arise for the development of basis functions: universal basis functions, based on the research of Silver and collaborators,[3,4] and adapted basis functions. Among the basis sets developed so far, it is important to highlight the work of Dunning and colleagues[5−10] as a reference in accurate molecular calculations. In 1986, seeking a new way to obtain basis functions, Mohallem et al.[11] introduced the generator coordinate Hartree–Fock method (GCHF). As an improvement to the GCHF, Barbosa and da Silva proposed the polynomial generator coordinate Hartree–Fock method (p-GCHF). In this new method, the choice of a nonequally spaced mesh is used to generate exponents for primitive functions. Because of this novelty, the obtained basis sets possess great flexibility and reduced number of primitive functions in the extended basis sets, without losing accuracy, when compared to the original GCHF.[12]

The basis sets used in this study satisfied, at the same time, the criteria of precision and applicability.[13,14]

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The precision criterion was obtained by comparing our results, on the atomic level, with numerical Hartree–Fock (NHF) calculations and, on the molecular level, by comparing the results obtained with Dunning's standard basis sets. The criterion of applicability was achieved because the p-GCHF method is capable of generating compact basis functions since the molecular calculations take less computation time when compared to Dunning's cc-PVQZ and cc-PV5Z basis sets,[12,15] without losing accuracy.

The purpose of this study is to present the accurate adapted Gaussian basis set developed by means of the p-GCHF method for hydrogen, zinc, and representative elements of the fourth period (K, Ca, Zn-Kr) with basis set 6Z valence quality[12,16] aiming to fill the lack of basis sets for accurate calculations with a low computational cost for these elements. Aiming at testing their quality we have applied these atomic basis sets to calculate the electronic total energies for the neutral atoms and their monovalent cations and anions, to determine the respective ionization potential for monovalent cation formation and electron affinity for monovalent anion formation. Our results are compared with those obtained by Bunge et al.[17] and Koga et al.[18] in studies at the NHF level, by Koga et al.[19] and Jorge and Fantin[20] with STF, by Saito[21] with B-spline functions, by Jorge et al.[22] with GTF, and experimental values.[23,24]

2. Results and discussion

Table 1 shows the Hartree–Fock ground-state total energies for H, K, Ca, Zn, and Ga-Kr obtained with the contracted and nonpolarized p-GCHF basis set, as well as those reported by Bunge et al.,[17] Koga et al.,[19] Saito,[22] and Jorge et al.[22] It is important to remark that these energies were calculated with our contracted basis sets (6Z) without diffuse functions and these values were compared with the extended basis sets results of the literature,[19,22] B-spline functions,[21] and NHF.[17] The results obtained with the p-CGHF basis set showed a relative error always lower than 6.0×10^{-5} % when compared with results reported by Bunge et al. (NHF),[17] Koga et al. (NHF),[19] Saito (B-spline),[21] and Jorge et al. (STF).[22] For H, our calculated value of energy was compared only with the results of Jorge et al.,[22] where the relative errors were always lower than 1.2×10^{-5} %.

As shown in Table 1, we can note that for the lightest elements (except for H 6Z basis sets), the p-GCHF basis sets provided better results than those published by Jorge et al.[22] Compared to numerical results, the energy differences were always lower than 1 $m\mathrm{E}_h$, reinforcing the p-GCHF[12] basis quality and the contraction method proposed by Davidson[25] and hence highlighting the accuracy of the developed p-GCHF basis set.

Table 2 shows the results obtained with nonpolarized p-GCHF basis sets for monovalent cations, as well as the results of Koga et al.,[19] Jorge and Fantin,[20] and Koga et al.[18] Analysis of Table 2 shows that our results were considerably more accurate than those presented by Jorge and Fantin,[20] who calculated with STF basis sets, and in many cases they were more accurate than those obtained by Koga et al. (NHF).[18] For Ga$^+$, our results were considerably more accurate than those obtained by Jorge and Fantin[20] and very close to those reported by Koga et al. (NHF).[18] Compared to Koga et al.[19] and Koga et al.,[18] our results were less accurate, but the relative errors were always lower than 7.0×10^{-5} %.

The results obtained for anions are shown in Table 3, where it can be noted that our results were better than those presented by Jorge and Fantin[20] with the STF basis set. The p-GCHF basis sets were prepared to describe atoms whose volumes are lower than that of the anions. This led to higher relative errors when compared to results for atoms and cations. However, the relative errors were always lower than 0.05% in comparison with the NHF results of Koga et al.[19] The only exception was for H$^-$ anion, which showed higher

Table 1. Hartree–Fock ground-state total energies for neutral H, K, Ca, Zn, and Ga-Kr.

Element	Configuration	State	Saito[21]	Jorge et al.[22]	p-GCHF - 5Z	p-GCHF- 6Z	p-GCHF - 7Z	Koga et al.[19]	Bunge et al.[17]
H	$1s^1$	^2S	-	-0.4999999325	-0.4999998870	-0.4999998870	-0.4999999911	-	-
K	$[Ar]4s^1$	^2S	-599.164786767	-599.1639648	-599.1646910	-599.1646250	-599.1645790	-599.1647868	-599.1647865
Ca	$[Ar]4s^2$	^1S	-676.758185925	-676.7578948	-676.7580940	-676.7580751	-676.7580332	-676.7581859	-676.7581857
Zn	$[Ar]4s^23d^{10}$	^1S	-1777.84811619	-1777.847613	-1777.847736	-1777.847706	-1777.847922	-1777.84816	-1777.84816
Ga	$[Ar]4s^23d^{10}4p^1$	^2P	-1923.26100961	-1923.259449	-1923.260503	-1923.260438	-1923.260404	-1923.261010	-1923.261009
Ge	$[Ar]4s^23d^{10}4p^2$	^3P	-2075.35973391	-2075.358884	-2075.359256	-2075.359229	-2075.359585	-2075.359734	-2075.359733
As	$[Ar]4s^23d^{10}4p^3$	^4S	-2234.23865428	-2234.237941	-2234.238202	-2234.237924	-2234.237909	-2234.238654	-2234.238654
Se	$[Ar]4s^23d^{10}4p^4$	^3P	-2399.86761170	-2399.866844	-2399.867136	-2399.866836	-2399.867066	-2399.867612	-2399.867611
Br	$[Ar]4s^23d^{10}4p^5$	^2P	-2572.44133316	-2572.440597	-2572.440833	-2572.440602	-2572.441230	-2572.441333	-2572.441332
Kr	$[Ar]4s^23d^{10}4p^6$	^1S	-2752.05497735	-2752.054104	-2752.054461	-2752.054283	-2752.054715	-2752.054977	-2752.054977

Table 2. Hartree–Fock ground-state total energies for monovalent cations for K, Ca, and Zn-Kr in E_h.

Z	Cation	Configuration	State	Koga et al.[18]	Jorge and Fantin[20]	p-GCHF - 5Z	p-GCHF - 6Z	p-GCHF - 7Z	Koga et al.[19]
19	K_+	$[Ar]$	^1S	-599.0177	-598.8312794	-599.0171688	-599.0171875	-599.0173805	-599.0175794
20	Ca^+	$[Ar]4s^1$	^2S	-676.5699	-676.2205126	-676.5699236	-676.5699060	-676.5698643	-676.5700126
30	Zn^+	$[Ar]4s^23d^9$	^2S	-1777.568	-1777.246545	-1777.567199	-1777.567145	-1777.567350	-1777.567545
31	Ga^+	$[Ar]4s^23d^{10}$	^1S	-1923.065	-1922.617722	-1923.059266	-1923.059202	-1923.059145	-1923.059722
32	Ge^+	$[Ar]4s^23d^{10}4p^1$	^2P	-2075.084	-2074.463491	-2075.086021	-2075.085997	-2075.085888	-2075.086491
33	As^+	$[Ar]4s^23d^{10}4p^2$	^3P	-2233.887	-2233.027335	-2233.887880	-2233.887601	-2233.887655	-2233.888335
34	Se^+	$[Ar]4s^23d^{10}4p^3$	^4S	-2399.560	-2398.768574	-2399.558094	-2399.557797	-2399.557918	-2399.558574
35	Br^+	$[Ar]4s^23d^{10}4p^4$	^3P	-2572.046	-2571.367211	-2572.044702	-2572.044472	-2572.045116	-2572.045211
36	Kr^+	$[Ar]4s^23d^{10}4p^5$	^2P	-2751.569	-2750.981394	-2751.566867	-2751.566742	-2751.567129	-2751.567394

relative errors, but lower than 0.6%. A higher relative error for this anion was expected because its radius is approximately twofold that of neutral H and, therefore, the H^- volume is almost eight times larger than that of the neutral atom.[23] The results of Koga et al.[19] were more accurate because, besides having been obtained from NHF calculations, their basis sets were augmented with diffuse functions.

Table 4 shows the nonrelativistic CISD ground-state total energies for H, K, and Ca, Zn-Kr elements obtained with polarized p-GCHF basis set 6Z - 2($l+$ 1)1($l+$ 2) and 6Z - 3($l+$ 1)1($l+$ 2)). Analyzing Table 4, it can be observed that the nonrelativistic energies description became more precise when the valence zone description was improved by increasing the number of polarization functions.

Tables 5 and 6 show ionization potential (IP) and electron affinities (EAs), respectively, in electronvolts (eV), calculated with nonpolarized 6Z and polarized 6Z - 2($l+$ 1)1($l+$ 2) and 6Z - 3($l+$ 1)1($l+$ 2) and experimental data.[24] Table 5 shows that IP calculations achieved accurate results, considering the fact that those basis sets were generated by optimization of neutral atoms and the influence of polarization functions on IPs was very small. Table 6 shows that only for Ga and As elements the polarization functions imposed significant influence on the calculated EAs and the values obtained with the polarized basis set were approximate to the experimental values. These observations reinforce the fact that polarization functions are important only in molecular calculations.

Figures 1 and 2 show IPs and EAs, respectively, obtained with p-GCHF - 6Z - $3(l+$ 1)1($l+$ 2) basis sets, the NHF results obtained by Koga et al.,[19] and experimental data versus atomic number (the behavior is exactly the same as for the other developed basis sets).
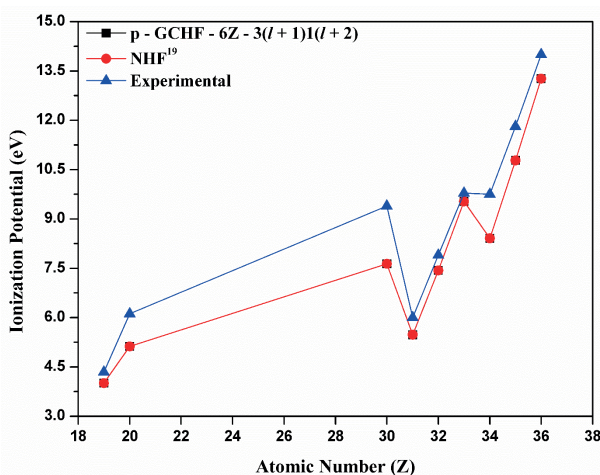

Figure 1. Ionization potential (IP) versus atomic number.

Table 5 and Figure 1 indicate that the results obtained with p-GCHF - 6Z - 3(l+1)1(l+2) basis sets were very close to the experimental values and followed the periodic behavior, including the modification on the trend due to the pairing of the $4p$ electrons in As to Se. The IP accuracy achieved in this study was the same as that obtained by Koga et al.[19] with NHF.

By analyzing Table 6 and Figure 2, it is observed that EAs were not accurately predicted when compared to experimental data. Positive values for EAs were obtained for some elements, but the p-CGHF results followed the experimental trend observed. The results obtained for EAs were expected because the calculation was performed with optimized basis sets for neutral atoms and not for anions. Therefore, the basis sets were

Table 3. Hartree–Fock ground-state total energies for monovalent anions for H, K, and Ga-Br in E_h.

Z	Anion	Configuration	State	Jorge and Fantin[20]	p-GCHF - 5Z	p-GCHF - 6Z	p-GCHF - 7Z	Koga et al.[19]
1	H⁻	$1s^2$	¹S	-0.487925434O	-0.4852114542	-0.4853550634	-0.4865983569	-0.4879297344
19	K⁻	$[Ar]4s^2$	¹S	-598.8847170	-599.1528151	-599.1528348	-599.1549787	-599.1619170
31	Ga⁻	$[Ar]4s^23d^{10}4p^2$	³P	-1922.667381	-1923.254349	-1923.254285	-1923.255442	-1923.260381
32	Ge⁻	$[Ar]4s^23d^{10}4p^3$	⁴S	-2074.419742	-2075.392010	-2075.391998	-2075.392457	-2075.394742
33	As⁻	$[Ar]4s^23d^{10}4p^4$	³P	-2233.389940	-2234.218366	-2234.218082	-2234.219373	-2234.222940
34	Se⁻	$[Ar]4s^23d^{10}4p^5$	²P	-2399.361726	-2399.902195	-2399.901933	-2397.681461	-2399.904726
35	Br⁻	$[Ar]4s^23d^{10}4p^6$	¹S	-2571.919273	-2572.533720	-2572.533479	-2572.535485	-2572.536273

Table 4. Nonrelativistic CISD ground state total energies for H, K, Ca, and Zn-Br atoms in E_h.

Z	Element	Configuration	State	p-GCHF - 5Z - 2(l+1) 1(l+2)	p-GCHF - 6Z - (l+1) 1(l+2)	p-GCHF - 6Z - (l+1) 1(l+2)	p-GCHF - 7Z - (l+1) 1(l+2)
1	H	$1s^1$	²S	-0.4999998870	-0.4999998871	-0.4999998871	-0.4999997274
19	K	$[Ar]4s^1$	²S	-599.1643576	-599.1643769	-599.1643810	-599.1645857
20	Ca	$[Ar]4s^2$	¹S	-676.7581074	-676.7580885	-676.7580891	-676.7580467
30	Zn	$[Ar]4s^23d^{10}$	¹S	-1777.847761	-1777.847726	-1777.847734	-1777.847930
31	Ga	$[Ar]4s^23d^{10}4p^1$	²P	-1923.260518	-1923.260459	-1923.260457	-1923.260414
32	Ge	$[Ar]4s^23d^{10}4p^2$	³P	-2075.359281	-2075.359256	-2075.359257	-2075.359133
33	As	$[Ar]4s^23d^{10}4p^3$	⁴S	-2234.238208	-2234.237939	-2234.237950	-2234.237914
34	Se	$[Ar]4s^23d^{10}4p^4$	³P	-2399.867140	-2399.866842	-2399.866867	-2399.867084
35	Br	$[Ar]4s^23d^{10}4p^5$	²P	-2572.440837	-2572.440615	-2572.440648	-2572.441239
36	Kr	$[Ar]4s^23d^{10}4p^6$	¹S	-2752.054467	-2752.054359	-2752.054405	-2752.054728

Table 5. Ionization potential (IP) obtained and experimental data for K, Ca, and Zn-Br elements in eV.

Element	p-GCHF - 5Z	p-GCHF - 5Z - $2(l+1)1(l+2)$	p-GCHF - 6Z	p-GCHF - 6Z - $2(l+1)(l+2)$	p-GCHF - 6Z - $3(l+1)(l+2)$	p-GCHF - 7Z	p-GCHF - 7Z - $2(l+1)(l+2)$	Experimental[24]
K	4.01428398	4.005075	4.011982	4.005039	4.005152	4.005478	4.005551	4.34066
Ca	5.12038086	5.120352	5.120346	5.120375	5.120309	5.120340	5.120377	6.11316
Zn	7.63380331	7.634077	7.634458	7.634721	7.634271	7.634762	7.634892	9.3942
Ga	5.47593242	5.475999	5.475923	5.476072	5.475986	5.476543	5.476737	5.9993
Ge	7.4351027	7.434553	7.435035	7.434545	7.434687	7.447674	7.435353	7.8994
As	9.53276478	9.531679	9.532767	9.531992	9.531829	9.530892	9.530811	9.7886
Se	8.40945739	8.409063	8.409380	8.409054	8.408974	8.412221	8.411878	9.75238
Br	10.7792495	10.77867	10.77926	10.77867	10.77875	10.77882	10.77888	11.81381
Kr	13.2681088	13.26814	13.26668	13.26766	13.26803	13.26791	13.26805	13.99961

Table 6. Electron Affinities (EA) obtained and experimental data for K, Ca, and Zn - Br elements in eV.

| Element	p-GCHF - 5Z	p-GCHF - 5Z - $2(l+1)1(l+2)$	p-GCHF - 6Z	p-GCHF - 6Z - $2(l+1)1(l+2)$	p-GCHF - 6Z - $3(l+1)1(l+2)$	p-GCHF - 7Z	p-GCHF - 7Z - $2(l+1)1(l+2)$	Experimental[24]
H	0.402414	0.402414	0.398506	0.398506	0.398511	0.364677	0.364670	-0.754195
K	0.323158	0.314088	0.320829	0.314077	0.306309	0.261238	0.261420	-0.50147
Ga	0.167440	0.144434	0.167436	0.141383	0.153875	0.135026	0.116624	-0.43
Ge	-0.891274	-0.890588	-0.891686	-0.890963	-0.888748	-0.894487	-0.906774	-1,232712
As	0.539761	0.509306	0.539916	0.509733	0.507978	0.504376	0.485140	-0,814
Se	-0.954000	-0.953887	-0.955038	-0.954889	-0.954789	-0.972292	-0.971689	-2,02067
Br	-2.527624	-2.542343	-2.527304	-2.542176	-2.540062	-2.564816	-2.567834	-3,363588
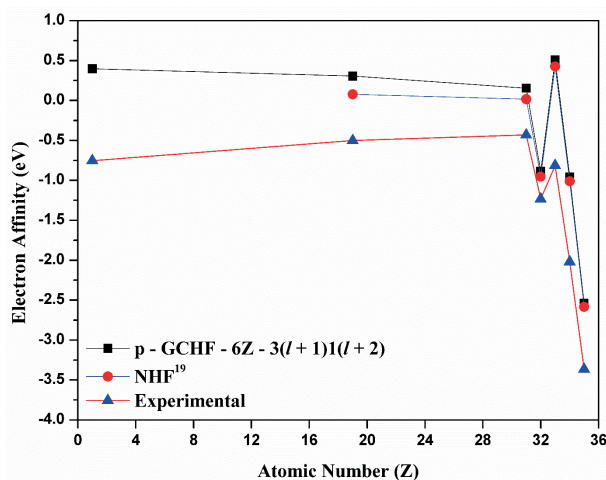
Figure 2. Electron affinity (EA) versus atomic number.

prepared to describe the atomic volume, which is much lower than the anion volume, and this led to less accurate results compared to experimental data. Our results, however, were the same obtained by Koga et al.[19] with NHF approximation for the heavier elements and followed the same trend found in experimental data, reaffirming the p-GCHF basis sets quality. The deviation found in the IP and EA results regarding the experimental data could be assigned to the incompleteness of the basis sets and the incomplete description of the electronic correlation and, specifically, the absence of diffuse function in the case of anions.

IP and EA results were not very sensitive to variation in the addition of polarization functions, where the difference in accuracy was negligible. This strengthens the fact that such parameters are only important in molecular calculations.[26]

In conclusion, the p-GCHF basis sets provided energies for atoms, cations, anions, IP, and EA as accurate as those described in the literature with NHF, STF, and B-spline type functions. We achieved the description of the periodicity in the same way as the experimental results for IPs and EAs. In addition, it was possible to prove that the use of basis sets with polarization functions does not improve IPs and EAs significantly; this procedure is important in molecular calculations only. The differences obtained for anions and EA calculations were attributed to the fact that the basis sets have been calibrated for atoms and the lack of diffuse functions could be assigned to the greater source of deviation. In this way, this study affirms the flexibility shown by the basis sets generated by p-GCHF methodology.

3. Experimental

For the elements studied, the size of extended basis sets developed by the p-GCHF method is as follow: 12s Gaussian functions for H, $22s14p$ for K and Ca, $22s14p10d$ for Zn, and $22s16p10d$ for Ga-Kr.[16] After the development of the extended basis set for each atom considered, we proceeded to the contraction step of the basis sets in accordance with the methodology proposed by Davidson[25] and implemented it in the CONTRACT package,[27] generating 6Z quality basis sets in the valence.[16] As a quality criterion for these atomic basis sets, extended and contracted, we imposed an error on them, considering nonrelativistic electronic total energies lower than 1 mHartree $(1\ \mathrm{m}E_h)$[16] or less when compared to NHF results.[17] The calculations for the extended and contracted sets were performed with the computational package GAMESS[28] using the generalized valence

bond method. All basis sets applied in this study were obtained by using polynomials with degree three, since this choice produces high-quality results and reduces computational time during the optimization steps.

The polarization functions were obtained through post-Hartree–Fock configuration interaction calculation, CISD method, performed with the GAUSSIAN 2003 [29] program. After this procedure, we obtained the following contracted and polarized basis set: $2(l+1)1(l+2)$, $3(l+1)1(l+2)$ and $3(l+1)2(l+2)1(l+3)$ for 6Z. In the notation here adopted, l is the angular quantum number of the last occupied atomic orbital in the ground state of the element. In this way, we developed 3 different basis sets for each element, named p-GCHF - 6Z - x, of different polarization basis sets (x). [16]

For the determination of IP and EA values for each basis set, the following criteria were adopted:

$$IP = E_{cation} - E_{atom}$$

$$EA = E_{anion} - E_{atom}$$

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