Relativistic Prolapse-Free Gaussian Basis Set of Quadruple-ζ Quality: (aug-)RPF-4Z. I. The *s*- and *p*-Block Elements

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Ⓢ *Supporting Information*

ABSTRACT: This study reports a new relativistic prolapse-free Gaussian basis set series of quadruple-ζ quality, RPF-4Z, and an augmented version that includes extra diffuse functions, aug-RPF-4Z, for all the s- and p-block elements. The relativistic adapted Gaussian basis sets (RAGBSs), which are free of variational prolapse, were used as the starting primitive sets. Exponents of correlating/polarization functions were taken from a polynomial version of the generator coordinate Dirac−Fock (p-GCDF) method, in which the previously optimized RAGBS parameters are applied. By using such procedure we aimed to reduce the computational demand of these sets in comparison with fully optimized ones. The effect of these basis set increments on the correlation energy was evaluated by atomic multireference configuration interaction calculations with single and double excitations out of the valence shell. Finally, atomic and molecular calculations of fundamental properties (bond lengths, vibrational frequencies, dipole moments and electron affinities) corroborate the quadruple-ζ quality of these new sets that are also about half-time-consuming than the correspondent Dyall's v4z sets. The read-to use format of these (aug-)RPF-4Fz sets are available as Supporting Information files and can also be found at http://basis-sets.iqsc.usp.br/.
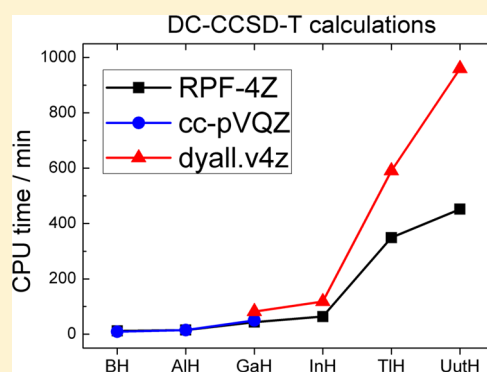
1. INTRODUCTION

The four-component codes now available for treating heavy element-containing-systems,[1−3] along with the rapid enhancement in computational power that took place in the last few decades, have largely increased the interest in developing relativistic basis sets.[4−45] Among this variety, the most successful series are probably those from Dyall,[34−45] which are complementary to the nonrelativistic correlation-consistent sets of Dunning and co-workers.[46−55]

However, relativistic basis sets are usually not free of variational prolapse,[26,56] a deficiency that appears as a result of neglecting the minimax theorem of Talman[57] during exponent optimizations. This problem can be detected by increases in the Dirac−Fock−Coulomb (DFC) energy results following the addition of tighter functions to a given set or, in the worst cases, by DFC energy values slightly lower than the correspondent numerical ones.[58] Such basis set inadequacy is usually noticed in the $s_{1/2}$ and $p_{1/2}$ atomic orbital symmetries[56] and becomes more relevant as the atomic number increases.[29−31] Thus, questionable results may be obtained for properties particularly sensitive to the description of innermost atomic regions in heavy and superheavy element-containing-compounds, exactly the ones that are the main concern of relativistic quantum chemistry studies. Obviously, due to the orthogonality between the spinors,[59,60] the prolapse might also affect properties that are more related to the valence electrons.[61]

Recently, *prolapse-free* relativistic adapted Gaussian basis sets (RAGBSs) were developed for all elements from $Z = 1$ up to Z

= 118.[29−31] In summary, for a given w angular symmetry, each RAGBS Gaussian-type function exponent, $\gamma_i^{(w)}$, is obtained through a polynomial version of the generator coordinate Dirac−Fock method (p-GCDF)[62] truncated at third order,

$$\frac{\ln \gamma_i^{(w)}}{\alpha} = \Theta_{\min}^{(w)} + \Delta\Theta_1^{(w)}(i-1) + \Delta\Theta_2^{(w)}(i-1)^2 + \Delta\Theta_3^{(w)}(i-1)^3 \tag{1}$$

where $i = 1, 2,..., N$, with N being the number of discretization points, α is a scaling parameter (6.0), whereas the $\Theta_{\min}^{(w)}$ and $\Delta\Theta_{q=1,2,3}^{(w)}$ parameters correspond, respectively, to the initial point of the mesh and the increment of order q applied to obtain discretization points. The careful adjustment of these parameters allowed overwhelming the prolapse problem with basis sets of very competitive sizes while keeping the deviations with respect to numerical results in only a few miliHartree (mE$_h$). Furthermore, these RAGBSs have been successfully used in determining nuclear electric quadrupole moments (NQMs),[63−67] a tough test for accurate basis sets.

Hence, by adopting the RAGBSs as a starting point, we aimed the development of a new series of relativistic prolapse-free Gaussian basis sets of quadruple-ζ quality (RPF-4Z), which is proposed to be competitive with the well-known quadruple-ζ sets of Dyall and Dunning. This process involved the addition

of functions to deal with the correlation and polarization effects of the valence electrons. Additionally, we also indicate an augmented set (aug-RPF-4Z) with extra diffuse functions to be used as needed. For now, (aug-)RPF-4Z for all the s- and p-block elements from $Z = 1$ up to $Z = 118$ are presented.

2. GENERAL CONSIDERATIONS

All calculations addressed here were carried out in the DIRAC12[1] package by means of the relativistic four-component Dirac-Coulomb (DC) Hamiltonian. The Gaussian nuclear model has been used along with the default speed of light value of 137.0359998 atomic units (au). The (SS|SS) two-electron integrals were replaced by an interatomic correction to reduce the computational demand.[68] Moreover, all basis sets were used in their uncontracted form.

At the RAGBS increment stage, atomic multireference configuration interaction calculations with single and double substitutions (DC-MRCISD) were performed through the direct relativistic configuration interaction (DIRRCI) module within DIRAC12. The Davidson correction has been also included when available. The active space was set so as to include all occupied spinors of the valence shell and the virtual spinors with energy up to 20.0 au. In addition, all substitutions within the valence electrons and spinors were allowed, whereas the reference determinants have been obtained through the Abelian symmetry group at each atomic ground level.[69] Regarding hydrogen and the alkaline metals, the respective calculations were done for the MH molecules (for M = hydrogen or an alkaline metal) in their equilibrium ground state geometry[69] (with exception of the FrH molecule, for which the bond length was assumed as 2.6 Å).

Further molecular calculations for evaluation purposes also considered the Coupled Cluster approach with iterative single and double excitations along with a perturbative correction for triple substitutions (DC−CCSD-T). Bond lengths and vibrational frequencies were found from a fourth order polynomial adjustment given by five DC−CCSD-T energy values around the minimum in the potential energy curve. These curves were determined on geometries given by atomic displacements of 0.01 Å nearby the experimental equilibrium bond length. Moreover, molecular dipole moments at the experimental equilibrium geometries were obtained through the sum of the analytic DFC value with DC−CCSD-T electron correlation contributions given by the finite-difference technique in a two point form,

$$\left(\frac{\partial E(\lambda)}{\partial \lambda}\right)_0 \approx \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \tag{2}$$

where E is the electron correlation energy and λ is the field strength used here as 1×10^{-6} au. The active space for these calculations of molecular properties and electron affinities was delimited to include all spinors with energy from −5 up to 20 au.

3. BASIS SET AUGMENTATION WITH CORRELATING/POLARIZATION FUNCTIONS

First, since the RAGBSs and the primitive composition of the cc-pVQZ and dyall.v4z sets have similar sizes, a quadruple-ζ type of increment was an evident choice to be pursued. However, instead of applying the usual procedure of optimizing the function exponents to treat electron correlation and polarization effects, we adopted a proposal that resembles the

procedure of Sadlej et al.[70−73] and is related to the idea of dual-family basis sets.[74] Thus, the exponents for the Gaussian functions of w angular symmetries not considered in the RAGBSs, $\gamma_i^{(w)}$, were generated by applying the previously optimized RAGBS parameters of the respective $w−2$ symmetry, $\Theta_{min}^{(w-2)}$ and $\Delta\Theta_{q=1,2,3}^{(w-2)}$, into eq 1. By using this procedure, we aimed to reduce the number of small component functions of further atomic and molecular calculations in accordance with the kinetic balance condition.[75,76] This will lead to a reduction of the computational cost in comparison with fully optimized exponent sets. At last, by varying the value of i, the individual effect of these given functions on the correlation energy was evaluated through atomic DC-MRCISD calculations. For clarification, an example of this procedure is discussed in the next subsection, while the particularities of the remaining elements are commented in the subsections 3.2 and 3.3.

3.1. Chlorine Example. The RAGBS for the chlorine atom includes only functions of s and p symmetries. In this case, d_i and g_i functions were determined by applying the previously optimized $\Theta_{min}^{(s)}$ and $\Delta\Theta_{q=1,2,3}^{(s)}$ parameters into eq 1 for different values of i, whereas the f_i functions were provided by the $\Theta_{min}^{(p)}$ and $\Delta\Theta_{q=1,2,3}^{(p)}$ parameters. The DC-MRCISD results from these increments are displayed in Table 1. First, by starting with the d_i functions, one can see that there is a clear minimum in energy on addition of d_3. Moreover, the effect of these functions on the total energy smoothly vanishes as the exponent of d_i becomes tighter or more diffuse than that of d_3. Thus, the three d_i functions with the largest individual effects on the total energy (d_2, d_3, and d_4) were added to the starting RAGBS. Next, by using this RAGBS+3d intermediate set, the same procedure was repeated for f functions. Again, a similar pattern in the energy variation is noticed and therefore the two f functions that resulted in the largest deviations with respect to the results of the previous set (f_3 and f_4) are selected to compose a new intermediate set, RAGBS+3d+2f. Finally, g functions were tested on addition to the latter intermediate set and the one with the largest contribution to the total energy (g_3) was chosen.

Furthermore, since the RAGBSs were determined through DFC calculations, extra functions of same angular symmetries as the ones already present in the initial set could be necessary for a better description of correlation and polarization effects. In such manner, s_i and p_i chlorine functions, for $i \leq 0$, were extrapolated by means of their respective parameters. However, none of these functions led to significant variations on DC-MRCISD energy results of chlorine and thereby were not included.

Hence, the final basis set (RPF-4Z) of chlorine is composed by the original RAGBS complemented with 3d (0.3616155587, 0.8530294661, and 1.917389540), 2f (0.5771740891 and 1.245183385), and 1g (0.8530294661) functions. Further calculations have shown that the correlating/polarization (C/P) set is well balanced even without any exponent optimization. The net effect of a fourth d, a third f, a second g, or an additional h function (following the energy lowering criteria) resulted in similar variations of −1.4, −1.3, −0.9, and −2.2 mE$_h$, respectively. Another aspect that also corroborates the methodology used here is that these exponents for the C/P functions of the RPF-4Z set closely resemble the fully optimized ones of the cc-pVQZ set,[48] which likewise includes 3d (0.254, 0.628 and 1.551), 2f (0.423 and 1.089), and 1g (0.827) functions.

Table 1. Basis Set Augmentation Study for the Cl Atom[a]

basis set	exponent	DC-MRCISD (E_h)	ΔE (mE_h)
RAGBS		−460.982864	
$+d_{-2}$	$5.371783921 \times 10^{-03}$	−460.982866	−0.001
$+d_{-1}$	$1.780308607 \times 10^{-02}$	−460.982925	−0.061
$+d_0$	$5.301398833 \times 10^{-02}$	−460.984341	−1.477
$+d_1$	$1.439401121 \times 10^{-01}$	−461.001660	−18.796
$+d_2$[b]	$\mathbf{3.616155587 \times 10^{-01}}$	−461.062221	−79.367
$+d_3$[b]	$\mathbf{8.530294661 \times 10^{-01}}$	−461.070612	−87.748
$+d_4$[b]	$\mathbf{1.917389540 \times 10^{00}}$	−461.005161	−22.296
$+d_5$	$4.167386790 \times 10^{00}$	−460.983933	−1.068
$+d_6$	$8.887961105 \times 10^{00}$	−460.982948	−0.084
$+d_7$	$1.887570142 \times 10^{01}$	−460.982864	0.000
RAGBS+3d[c]		−461.104221	−121.356
$+f_{-1}$	$9.881437185 \times 10^{-03}$	−461.104221	0.000
$+f_0$	$3.354028156 \times 10^{-02}$	−461.104263	−0.042
$+f_1$	$9.743778804 \times 10^{-02}$	−461.105667	−1.446
$+f_2$	$2.492046580 \times 10^{-01}$	−461.117111	−12.890
$+f_3$[b]	$\mathbf{5.771740891 \times 10^{-01}}$	−461.135973	−31.753
$+f_4$[b]	$\mathbf{1.245183385 \times 10^{00}}$	−461.127817	−23.696
$+f_5$	$2.573887239 \times 10^{00}$	−461.109572	−5.351
$+f_6$	$5.243597096 \times 10^{00}$	−461.104541	−0.320
$+f_7$	$1.082945494 \times 10^{01}$	−461.104221	0.000
RAGBS+3d+2f[d]		−461.140910	−36.690
$+g_{-1}$	$1.780308607 \times 10^{-02}$	−461.140910	0.000
$+g_0$	$5.301398833 \times 10^{-02}$	−461.140923	−0.013
$+g_1$	$1.439401121 \times 10^{-01}$	−461.141453	−0.542
$+g_2$	$3.616155587 \times 10^{-01}$	−461.145700	−4.790
$+g_3$[b]	$\mathbf{8.530294661 \times 10^{-01}}$	−461.150164	−9.254
$+g_4$	$1.917389540 \times 10^{00}$	−461.145167	−4.256
$+g_5$	$4.167386790 \times 10^{00}$	−461.141328	−0.417
$+g_6$	$8.887961105 \times 10^{00}$	−461.140910	0.000

[a]The original RAGBS[29] is incremented with functions of $\gamma_i^{(w)}$ exponents given by the $\Theta_{min}^{(w-2)}$ and $\Delta\Theta_{q=1,2,3}^{(w-2)}$ parameters applied into eq 1. The functions that resulted in the largest energy variations (ΔE) in DC-MRCISD calculations are chosen to compose the [3d 2f 1g] correlating/polarization set. [b]Functions chosen to compose the final correlating/polarization set (bolded exponents). [c]Basis set composed by the RAGBS and three selected d functions. The ΔE values displayed in the lines below, which refer to the inclusion of f functions, are given in relation to the total energy value obtained with this RAGBS+3d intermediate set. [d]Basis set composed by the RAGBS +3d set and the two selected f functions. The ΔE values displayed in the lines below are given in relation to the total energy value obtained with this RAGBS+3d+2f intermediate set.

3.2. p-Block Elements. The same methodology exemplified for chlorine was also applied to all atoms of the 2p- and 3p-block elements. Along that study, we have noticed that the selection of functions by means of their individual contributions to the total energy agrees for most of the cases with an alternative choice of functions by their combined effect. However, exceptions were found for elements in which one function of a given angular symmetry had to be selected between two functions with almost the same individual contribution to the total energy (differences of 1 mE_h or less). In such instances, the analysis of the combined effect was preferred over the individual contributions and the final set was composed by the *group* of functions with the largest contribution to the total energy.

The selected C/P functions for the 2p- and 3p-block elements are represented in Table 2 by means of the respective i labels associated with them. As one can notice, the i values that give rise to the chosen functions are almost the same throughout a period. Therefore, by starting from the lightest elements, a single turning point is found in each period: at the O and Cl elements. This is an advantage of the polynomials previously adjusted to obtain RAGBSs[29−31] which are also well-behaved along periods. In such manner, there is no reason to believe in any anomalous behavior in the i values along each of the next periods. This means that repeating the same work for all the p-block elements of remaining periods would be probably overindulgent and unnecessary. Thereby, the basis set increment study was further carried out for the 13- and 18-group elements only. From these points on, if necessary (when i values of the two elements in a given period are not the same for each angular symmetry), extra calculations were done until the turning point could be found. Then, the i values for the remaining atoms of that period were assumed as the same as either those for the element of the 13 or 18 groups.

Thus, following the quadruple-ζ increment-type for the 4p- and 5p-block elements,[34,35,38] which already include d functions in their RAGBS sets, we first proceeded to the determination of a [2f 1g] C/P set by using the same methodology applied to the elements of the first periods. Thus, f and g function exponents were obtained from the $\Theta_{min}^{(p)}/\Delta\Theta_{q=1,2,3}^{(p)}$ and $\Theta_{min}^{(d)}/\Delta\Theta_{q=1,2,3}^{(d)}$ parameters, respectively, and the most important functions were further selected from the DC-MRCISD energy values. Then, additional s, p, and d functions were also determined through extrapolations in eq 1 by means of their respective parameters for $i \leq 0$. DC-MRCISD results showed that only one diffuse d function has a significant contribution to the correlation energy. Hence, a group of [1d 2f 1g] functions was selected for the 4p- and 5p-block elements. These functions are discriminated in Table 3. Similarly to these previous cases, [1d 2f 1g] and [1s 1d 2f 1g] C/P sets were added to the RAGBSs of the 6p- and 7p-block elements, respectively. Such sets can be found in Table 4.

3.3. s-Block Elements. The C/P functions for hydrogen through beryllium were derived from their respective $\Theta_{min}^{(s)}$ and $\Delta\Theta_{q=1,2,3}^{(s)}$ parameters. The analysis indicated that a [3p 2d 1f] set of functions is satisfactory for H and He. Regarding the 2s

Table 2. Values of i To Be Used in the Polynomial Expansion Shown in Equation 1 along with the Respective Previously Optimized Parameters[a] **To Obtain the Correlating/Polarization Functions of the RPF-4Z Sets for the 2p- and 3p-Block Elements**

w	B	C	N	O	F	Ne	Al	Si	P	S	Cl	Ar
d	2−4	2−4	2−4	2−4	2−4	2−4	1−3	1−3	1−3	1−3	2−4	2−4
f	4, 5	4, 5	4, 5	3, 4	3, 4	3, 4	3, 4	3, 4	3, 4	3, 4	3, 4	3, 4
g	4	4	4	3	3	3	3	3	3	3	3	3

[a]$\Theta_{min}^{(s)}$ and $\Delta\Theta_{q=1,2,3}^{(s)}$ parameters are used for d and g functions, while $\Theta_{min}^{(p)}$ and $\Delta\Theta_{q=1,2,3}^{(p)}$ parameters are applied for f functions. Such parameters are found in ref 29.

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Table 3. Values of i To Be Used in the Polynomial Expansion Shown in Equation 1 Along with the Respective Previously Optimized Parameters[a] To Obtain the Correlating/Polarization Functions of the RPF-4Z Sets for the 4p- and 5p-Block Elements

w	Ga	Ge	As	Se	Br	Kr	In	Sn	Sb	Te	I	Xe
d	0	0	0	0	0	0	0	0	0	0	0	0
f	2, 3	2, 3	2, 3	2, 3	2, 3	3, 4	3, 4	2, 3	2, 3	2, 3	2, 3	2, 3
g	1	1	1	1	1	1	1	1	1	1	1	1

[a]$\Theta_{min}^{(d)}$ and $\Delta\Theta_{q=1,2,3}^{(d)}$ parameters are used for d and g functions, while $\Theta_{min}^{(p)}$ and $\Delta\Theta_{q=1,2,3}^{(p)}$ parameters are applied for f functions. Such parameters are found in ref 29.

Table 4. Values of i To Be Used in the Polynomial Expansion Shown in Equation 1 Along with the Respective Previously Optimized Parameters[a] To Obtain the Correlating/Polarization Functions of the RPF-4Z Sets for the 6p- and 7p-Block Elements

w	Tl	Pb	Bi	Po	At	Rn	Uut	Fl	Uup	Lv	Uus	Uuo
s							0	0	0	0	0	0
d	0	0	0	0	0	0	0	0	0	0	0	0
f	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0
g	2	2	2	2	2	2	2	2	2	2	2	2

[a]$\Theta_{min}^{(w)}$ and $\Delta\Theta_{q=1,2,3}^{(w)}$ parameters are used for functions with $w = s$, d, and f, while $\Theta_{min}^{(d)}$ and $\Delta\Theta_{q=1,2,3}^{(d)}$ parameters are applied for g exponents. Such parameters are found in refs 30 and 31.

Table 5. Values of i To Be Used in the Polynomial Expansion Shown in Equation 1 Along with the Respective Previously Optimized Parameters[a] To obtain the Correlating/Polarization Functions of the RPF-4Z Sets for the s-Block Elements

w	H[b]	He[b]	Li[b]	Be[b]	Na	Mg	K	Ca	Rb	Sr	Cs	Ba	Fr	Ra
p	3−5	2−4	1−8	1−8	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0
d	3, 4	3, 4	3−5	3−5	2−4	2−4	1−7	1−7	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0
f	4	4	3, 4	3, 4	0, 1	0, 1	0−2	0−2	0−2	0−2	0−3	0−3	−2−0	−2−0
g		3	4	2	3	2	3	−1	−1	−1	−1	−1	0	

[a]$\gamma_i^{(w)}$ function exponents of w angular symmetries already considered in the original RAGBSs are taken from their respective $\Theta_{min}^{(w)}$ and $\Delta\Theta_{q=1,2,3}^{(w)}$ parameters, while the function exponents of higher angular symmetries are given by the $\Theta_{min}^{(w-2)}$ and $\Delta\Theta_{q=1,2,3}^{(w-2)}$ parameters. All these parameters are found in refs 29−31. [b]All exponent functions are obtained from $\Theta_{min}^{(s)}$ and $\Delta\Theta_{q=1,2,3}^{(s)}$ parameters.

Table 6. Average Absolute Deviations (AADs) and the Maximum Absolute Errors (MAEs) Determined with the Given Basis Sets in DC−CCSD-T (for r_e, ω_e, and μ)[a] and DC-MRCISD Calculations (for EA)[a] with Respect to Experimental Data[69,77]

	r_e (Å)		ω_e (cm^{-1})		μ (D)[b]		EA (eV)[c]	
basis sets	AAD	MAE	AAD	MAE	AAD	MAE	AAD	MAE
RPF-4Z	0.0033	0.0122	12	26	0.06	0.11	0.146	0.226
dyall.v4z[d]	0.0026	0.0053	20	60	0.09	0.22	0.142	0.202
dyall.v3z[d]	0.0047	0.0134	14	24	0.20	0.37	0.188	0.268
cc-pVQZ[e]	0.0067	0.0262	20	45	0.07	0.15	0.162	0.226
cc-pVTZ[e]	0.0076	0.0220	18	54	0.12	0.29	0.211	0.278

[a]The following molecules are considered for r_e, ω_e, and μ results: MH (M = Li, Na, K, Rb, and Cs), HX (X = F, Cl, Br, and I) and YF (Y = B, Al, Ga, In, and Tl). Halogens and group 13 atoms are analyzed for the EAs. [b]Does not include results for NaH, KH, RbH, CsH, and BF due to the lack of accurate experimental data. [c]This property was evaluated by applying the respective basis sets in their augmented form with diffuse functions. [d]These basis sets are not available for elements of the first three periods. Thus, the cc-pVQZ and cc-pVTZ sets of lighter atoms (H and F) are used along with the v4z and v3z sets, respectively. For the same reasons, results attributed to these sets do not enclose calculations for LiH, NaH, HF, HCl, BF, AlF, F, Cl, B, and Al. [e]These basis sets are only available for the elements up to the fourth period (with exception of potassium). Hence, results attributed to these sets do not enclose calculations for KH, RbH, CsH, HI, InF, TlF, I, In, and Tl.

elements, the proximity of the next $2p$ subshell requires that the basis sets of these elements be similar to the ones of the 2p-block elements. Hence, prior to the inclusion of the $[3d\ 2f\ 1g]$ set for Li and Be, p functions were added until no further significant variations had been noticed in the DC-MRCISD energy. In matter of the Na and Mg elements, $2p$ functions also had to be added along with the $[3d\ 2f\ 1g]$ set.

Concerning the basis sets for K and Ca, extra d functions had to be included prior to the $[2f\ 1g]$ set due to the proximity of a new subshell with d angular symmetry. Moreover, the diffuseness of the valence-shell in these cases also required

the inclusion of two p and one f extra functions for a better representation of polarization effects on binding. For similar reasons, the C/P sets for the RPF-4Z of 5s-, 6s-, and 7s-block elements are complemented with $[2p\ 2d\ 3f\ 1g]$, $[2p\ 2d\ 4f\ 1g]$, and $[2p\ 2d\ 3f\ 1g]$ sets of functions, respectively. All C/P sets for the s-block elements are displayed in Table 5.

3.4. Diffuse Functions. An augmented series with extra diffuse functions is also proposed in addition to the C/P sets by considering the exponents determined with an i value one unit smaller than those already used in the RPF-4Z sets for each angular symmetry. This alternative version is labeled here as

Table 7. Total CPU^a Time in Single-Point DC−CCSD-T Calculations along with Different Basis Sets

YH	RPF-4Z^b		dyall.v4z^c		cc-pVQZ^c	
	time	Y set size	time	Y set size	time	Y set size
BH	00:12:00	14s8p3d2f1g			00:09:21	12s6p3d2f1g
AlH	00:15:26	18s13p3d2f1g			00:15:05	16s11p3d2f1g
GaH	00:44:05	21s17p11d2f1g	01:22:15	30s21p13d2f1g	00:50:33	21s16p12d2f1g
InH	01:03:39	25s21p14d2f1g	01:57:44	33s27p18d2f1g		
TlH	05:48:38	30s27p17d13f1g	09:51:28	34s31p21d14f1g		
UutH	07:32:12	34s30p20d16f1g	15:59:53	35s35p24d16f1g		

^{a}Intel Xeon X5650 CPU (12 M Cache, 2.67 GHz). ^{b}The RPF-4Z set of hydrogen is composed by 8s3p2d1f functions. ^{c}The cc-pVQZ (6s3p2d1f functions) set was used for hydrogen.

aug-RPF-4Z. These sets are recommended for anionic systems and for a better description of weak and long-range interactions.

4. MOLECULAR AND ATOMIC TESTS

In this section, we first discuss the results of molecular DC−CCSD-T calculations carried out with the RPF-4Z sets for equilibrium distances (r_e), harmonic vibrational frequencies (ω_e) and dipole moments (μ). These values are also compared with those from cc-pVQZ and cc-pVTZ sets of Dunning for lighter elements, along with results that considered v4z and v3z sets of Dyall for heavier atoms (combined with the respective sets of Dunning for hydrogen and fluorine). This investigation included simple diatomic molecules such as MH (M = Li, Na, K, Rb and Cs), HX (X = F, Cl, Br, and I) and YF (Y = B, Al, Ga, In, and Tl). Furthermore, electron affinities (EAs) of halogens and group 13 elements were also determined by using the augmented versions (which include extra diffuse functions) of these basis sets through differences in the total DC-MRCISD energy between the neutral and anionic forms of these atoms. Average absolute deviations (AADs) and the maximum absolute errors (MAEs) with respect to experimental data[69,77] are shown in Table 6 (detailed results are displayed in Tables S1−S4 in the Supporting Information). As expected, there is a clear pattern of improvement in general results along with increasing basis set quality. It is also evident that the values from the (aug-)RPF-4Z sets are in excellent accordance with those of dyall.(a)v4z and (aug-)cc-pVQZ ones.

Another important consideration to be taken in the development of basis sets is the related demand for computational resources. Therefore, we compared the CPU time in single-point DC−CCSD-T calculations for the YH molecules (Y = 13 group elements) with the RPF-4Z, cc-pVQZ, and dyall.v4z sets. These data are displayed in Table 7 along with basis set sizes. From these results one can notice that the RPF-4Z sets are about half-time-consuming than the dyall.v4z ones, which is primarily in line with the respective basis set sizes. However, part of this reduction can also be attributed to the methodology applied to determine the C/P sets (see the first paragraph of section 3). For instance, although the RPF-4Z and the cc-pVQZ sets have almost the same size for the GaH case, the RPF-4Z is about 15% faster than the cc-pVQZ set. Such difference must be even more pronounced when (SS|SS) two-electron integrals are explicitly considered. In addition, the discrepancy in CPU time between results of RPF-4Z and dyall.v4z will be even larger for calculations in which all atoms are addressed by the Dyall's sets (it is well-known that the dyall.v4z sets are larger than the respective cc-pVQZ ones for the elements in which both alternatives are available, see for example, the basis sets for gallium). Furthermore, this outstanding RPF-4Z performance in atomic and molecular calculations along with its low computational cost might be a consequence of a better arrangement of the polynomial-derived exponents of the p-GCDF methodology.

5. CONCLUSIONS

We presented the first part of an investigation concerned with the development of a new series of relativistic prolapse-free Gaussian basis sets of quadruple-ζ quality, RPF-4Z. For now, all the s- and p-block elements from Z = 1 up to Z = 118 are addressed. The use of the RAGBSs as the starting primitive sets assures that the function exponents are well-disposed for an accurate description of the inner through the valence atomic regions while overwhelming the variational prolapse problem. By applying the RAGBS parameters of already available function symmetries to determine the correlating/polarization sets, in accordance with the kinect balance condition, a smaller number of integrals are generated on calculation in comparison with fully optimized sets.

Results from molecular and atomic calculations of fundamental properties attested the quadruple-ζ quality of these sets together with a CPU time reduction of about 50% in comparison with the Dyall's v4z sets. In addition, another advantage of the RPF-4Z is the possibility of easily obtaining extensions of these sets with extra tighter or more diffuse functions, or even functions of higher angular symmetries. This can be done by applying the RAGBS parameters available in refs 29−31 into the polynomial shown in eq 1 following the methodology described here. Besides, an augmented version with one extra diffuse function for each symmetry, aug-RPF-4Z, is already provided as this series can be used with anionic systems and for a more accurate description of weak and long-range interactions.

The extension of this series for the d- and f-block elements, along with additional sets for core−valence correlation effects, will be soon provided. Complete listings of the (aug-)RPF-4Z sets in ready-to-use format are available in the Supporting Information and are also provided at http://basis-sets.iqsc.usp.br/.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Detailed results of atomic and molecular properties (Tables S1−S4). RPF-4Z and aug-RPF-4Z in ready-to-use format. This material is available free of charge via Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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