Relativistic Prolapse-Free Gaussian Basis Set of Quadruple-ζ Quality: (aug-)RPF-4Z. II. The d-Block Elements
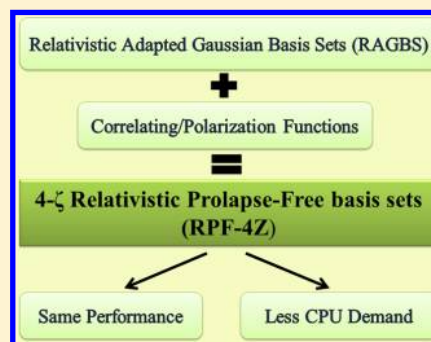
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S *Supporting Information*

ABSTRACT: A series of relativistic prolapse-free Gaussian basis sets of quadruple-ζ quality has been developed: (aug-)RPF-4Z. Here, we report the (aug-)RPF-4Z sets for all the d-block elements (Sc−Cn). Molecular calculations at the Coupled Cluster level showed a significant reduction in computational demand in comparison with other well-known relativistic quadruple-ζ sets. The (aug-)RPF-4Z sets in a ready-to-use format are available as Supporting Information and can also be found at http://basis-sets.iqsc.usp.br/.

Relativistic Adapted Gaussian Basis Sets (RAGBS)
+
Correlating/Polarization Functions
=
4-ζ Relativistic Prolapse-Free basis sets (RPF-4Z)

Same Performance Less CPU Demand

1. BASIS SET DEVELOPMENT

This is the second part of a research concerned with the development of quadruple-ζ relativistic prolapse-free Gaussian basis sets (RPF-4Z). First, we presented the RPF-4Z and its augmented version with extra diffuse functions, aug-RPF-4Z, for all the s- and p-block elements.[1] Now, we report the (aug-)RPF-4Z sets for the d-block elements. A similar procedure as that used for the main group elements is applied here; thus, one can seek for more detailed information about this methodology in Part I.[1] In summary, the relativistic adapted Gaussian basis sets (RAGBSs)[2−4] (the ones related to the experimental ground level configuration of the respective elements), which are free of variation prolapse, have been used as starting primitive sets. Then, correlating/polarization (C/P) function exponents of higher w angular symmetries, $\gamma_i^{(w)}$, were obtained by applying the RAGBS parameters of the respective $w-2$ angular symmetry into a polynomial version of the generator coordinate Dirac−Fock method (p-GCDF)[5] truncated at third order,

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

(1)

in which i = 1, 2,..., N, with N equal to the number of discretization points, α is a scaling parameter used here as 6.0, whereas the $\Theta_{\min}^{(w)}$ and $\Delta\Theta_{q=1,2,3}^{(w)}$ parameters relate to the initial point of the mesh and the increment of order q applied to determine discretization points, respectively. Thus, by means of such a methodology, in accordance with the kinetic balance condition,[6,7] we aimed to reduce the number of *small* functions

generated in further calculations, leading to a reduction in computational effort as demonstrated in ref 1. Additional functions of angular symmetries already presented in starting RAGBSs were also considered to better describe the correlation/polarization effects. In this case, the exponents of such functions were found by extrapolations from the RAGBS parameters of the respective symmetry by using $i \leq 0$ values in eq 1.

Thus, in order to achieve a quadruple-ζ type of increment (see, e.g., refs 8 and 9), we first pursued the best $[3f\,2g\,1h]$ and $[2g\,1h]$ sets of function exponents for the (3 and 4)d- and (5 and 6)d-block elements, respectively. This was done by analyzing the results of atomic multireference configuration interaction calculations with single and double substitutions (MRCISD) through the direct relativistic configuration interaction (DIRRCI) module within the DIRAC12 code.[10] The relativistic four-component Dirac−Coulomb (DC) Hamiltonian was applied in conjunction with the Gaussian nuclear model and the DIRAC12 default speed of light value, 137.0359998 atomic units (au). Moreover, (SS|SS)-type integrals were replaced by an interatomic correction in all calculations.[11] The Davidson correction was also applied when available. The active space was set in manner to include all $(n-1)d$ and ns (with n = 4−7) valence electrons and the virtual spinors with energy up to 20.0 au. All substitutions within the valence active space were allowed. The reference determinants were set by means of the Abelian symmetry group at each atomic ground level.[12]

Table 1. 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 (C/P) Functions of the RPF-4Z Sets for the d-Block Elements

	3d-block		4d-block		5d-block		6d-block	
w	Sc	Ti–Zn	Y–Zr	Nb–Cd[b]	Lu–Re	Os–Hg	Lr-Bh	Hs-Cn
p	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0	−1, 0
d	0	0	0	0	0	0	0	0
f	1−3	1−3	1−3	1−3	0	0	0	0
g	2, 3	3, 4	2, 3	3, 4	3, 4	3, 4	2, 3	3, 4
h	2	2	2	2	1	2	1	1

[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 obtained by applying the $\Theta_{min}^{(w-2)}$ and $\Delta\Theta_{q=1,2,3}^{(w-2)}$ parameters. All these RAGBS parameters are found in refs 2−4. [b]One extra s function ($i = 0$) was added to Pd.

As also commented in ref 1, the analysis of the C/P sets was carried out by examining the first and last atoms in each nd-block. Hence, we first added single groups of $3f_i$ (with $i = ..., 0−2, 1−3, 2−4, ...$) functions to the Scandium RABGS ([Ar]$3d4s^2$ ground configuration). The group that resulted in the largest reduction in the DC-MRCISD atomic energy, the $[f_{1−3}]$ set, was chosen to be included in the final set of this element. Then, groups of $2g$ functions were considered in the same manner as the f ones by comparison with results of this previous RAGBS +$3f$ set. In such a case, the g_2 and g_3 functions are selected. Concerning the individual h function, we adopted the same exponent as that of the intermediate f function previously added (f_2). Finally, as commented above, we also analyzed the effect of more diffuse s, p, and d functions in order to obtain a better description of correlation/polarization effects once RAGBSs were developed within a Dirac−Hartree−Fock (DHF) environment. The DC-MRCISD calculations pointed that $2p_i$ ($i = −1, 0$) and $1d_i$ ($i = 0$) functions result in energy variations similar to those observed with the previously discussed functions of higher angular symmetries. This means that these $2p$ and $1d$ functions must be as important to describe the correlation effects as the ones of the $[3f\ 2g\ 1h]$ set. Thus, they are required to keep the resulting final set well-balanced.

The same procedure was then applied to the heaviest element of the same block, zinc. However, the pair of g_3 and g_4 functions is now responsible for a larger DC-MRCISD energy decrease than that of the pair composed by g_2 and g_3 functions found previously for scandium. Hence, we proceeded to the search for the elements in which this particular $[g_{2,3}] \rightarrow [g_{3,4}]$ change occurs. This "turning point" was found when going from Sc through Ti, which means that the $[g_{2,3}]$ set is only indicated for Sc, while the $[g_{3,4}]$ set is better suitable for all the elements from Ti up to Zn, in agreement with findings from ref 1, based on the well-behaved RAGBS parameters derived from the exponential relation depicted in eq 1. Moreover, it was also noticed that the importance of the $[3f\ 2g\ 1h]$ set in DC-MRCISD results increases along the period in comparison with that of the extra $[2p\ 1d]$ one. However, although this feature is evident in energy values, it is not easy to determine how this affects the determination of other atomic and molecular properties. Thus, in order to maintain these sets with the same size along a given block and for safety reasons, the group of $[2p\ 1d]$ functions is kept for all elements of the 3d-block, composing the proposed $[2p\ 1d\ 3f\ 2g\ 1h]$ C/P final set for Sc−Zn.

The latter analyses were also done for the 4d-block elements. Similarly, a $[2p\ 1d\ 3f\ 2g\ 1h]$ C/P set was selected here. However, a single case had to be examined with more care. The RAGBS related to the unusual experimental ground level of

Palladium[12] ($^1S_0$) does not contain as diffuse s functions as the ones presented in the RAGBSs for its alternative configurations and for remaining elements of the same block. Therefore, we included one extra s function ($i = 0$) into the Pd set.

Concerning the 5d- and 6d-block elements, the $2g$ functions of the $[2g\ 1h]$ set were selected by a similar procedure as done for the previous elements. However, since the RAGBSs of 5d- and 6d-block atoms already include f functions, the individual h function exponent of the $[2g\ 1h]$ set was now also determined by DC-MRCISD calculations, that is, the f RAGBS parameters were applied and the energy decrease is analyzed. Moreover, additional $[2p\ 1d\ 1f]$ functions were again chosen for these elements due to their relevance for a better description of correlation/polarization effects. The i values indicated for the C/P functions of all the d-block elements are displayed in Table 1.

Finally, the RPF-4Z is simply obtained by adding the C/P sets related with the i values shown in Table 1 to the RAGBSs determined for the experimental ground level configuration of the respective elements. Basis set sizes account for $21s15p11d3f2g1h$, $25s19p14d3f2g1h$, $30s24p18d12f2g1h$, and $33s29p20d15f2g1h$ functions for the 3d-, 4d-, 5d-, and 6d-block elements, respectively (the Pd set includes also one extra s function). In addition, another version of these sets augmented with more diffuse functions is provided, aug-RPF-4Z. The diffuse function exponents in these aug-RPF-4Z sets were determined by applying i values one unit smaller than the ones already considered in the RPF-4Z sets for each angular symmetry. In addition, extra diffuse functions, tighter functions, or even functions of higher angular symmetries, which might be required for specific calculations, can be easily obtained and added to the (aug-)RPF-4Z sets by applying the RAGBS parameters into eq 1, following the procedure presented here. The ready-to-use format of the RPF-4Z and aug-RPF-4Z sets can be found as Supporting Information and at http://basis-sets.iqsc.usp.br/.

2. MOLECULAR TESTS

Finally, molecular properties of a few representative systems were determined to evaluate the RPF-4Z sets. The Coupled Cluster approach with iterative single and double excitations along with a perturbative correction for triple substitutions (DC-CCSD-T) was chosen to these calculations. The active space was set to enclose all spinors with energy from −3 through 20 au. Equilibrium distances (r_e) and harmonic vibrational frequencies (ω_e) were determined by a fourth order polynomial fit that included five points around the minimum in the potential energy curve. Dipole moments (μ) were obtained at the experimental equilibrium geometries[12]

Table 2. DC-CCSD-T Calculations of Bond Lengths (r_e), Harmonic Vibrational Frequencies (ω_e), Molecular Dipole Moments (μ), and Absolute Deviations with Respect to Experimental Data[a]

molecules	sets	r_e (Å)		ω_e (cm^{-1})		μ (D)[b]		time (h)[c]
		calc.	|dev.|	calc.	|dev.|	calc.	|dev.|	
CuH	RPF-4Z	1.452	**0.011**	1987	**45**	2.70		1.8
	cc-pVQZ	1.450	**0.013**	1981	**40**	2.76		1.3
CuF	RPF-4Z	1.739	**0.006**	625	**2**	5.32	**0.38**	4.9
	cc-pVQZ	1.737	**0.008**	630	**8**	5.27	**0.43**	3.4
AgH	RPF-4Z	1.604	**0.014**	1810	**50**	2.79		2.3
	dyall.v4z[d]	1.609	**0.009**	1789	**30**	2.78		17.3
AgF	RPF-4Z	1.977	**0.006**	520	**6**	5.97	**0.25**	6.2
	dyall.v4z[d]	1.976	**0.008**	525	**11**	5.80	**0.42**	33.3
AuH[e]	RPF-4Z	1.514	**0.010**	2354	**49**	1.27		11.1
AuF[e]	RPF-4Z	1.911	**0.007**	576	**17**	4.22		22.4

[a]The methodology used to obtain these properties is summarized in the text and is detailed in ref 1, whereas the experimental data is taken from refs 12 and 13. [b]Accurate experimental values could not be found for the molecules in which there is not a related deviation value. [c]Average CPU time demanded in single point calculations done in an Intel Xeon X5650 CPU (12 M Cache, 2.67 GHz). [d]As this series does not include sets for the elements of the first two periods, the cc-pVQZ set is applied for H and F. [e]Comparative calculations with the dyall.v4z sets are beyond our computational resources.

through application of an electrical field. More details about how these properties were calculated can be found in ref 1. The results were compared with experimental data[12,13] and theoretical values given by the nonrelativistic cc-pVQZ[8] and the relativistic dyall.v4z[9] sets (these sets were also kept in their uncontracted form and the small functions were generated through the kinetic balance condition[6,7]). These results are shown in Table 2 along with the average CPU time spent on single point calculations of each molecule. In general, it is noticed that all basis sets show larger deviations with respect to experimental results than the ones obtained for the main group element molecules investigated in ref 1, which is expected when a single-reference method is used for transition-element-containing molecules (see, e.g., ref 14). However, the main conclusion taken from Table 2 is that the RPF-4Z sets present overall results of same quality as those from the other well-known quadruple-ζ counterparts, along with a significant reduction in CPU demand is comparison with the relativistic dyall.v4z sets. Such a difference in "computational cost" can be mainly attributed to smaller basis set sizes of the RPF-4Z, and to the methodology applied here, which results in a reduced number of small functions for the (aug-)RPF-4Z in comparison with fully optimized basis sets. For example, while the RPF-4Z for Ag generates 247 large ($25s19p14d3f2g1h$) and 505 small ($19s39p19d14f3g2h1i$) functions, the dyall.v4z set for the same element comprises 372 large ($33s25p17d6f4g2h$) and 831 small ($25s50p31d21f8g4h2i$) functions. Although one can reduce the computational demand of dyall.v4z sets for these elements by retrieving, for example, the $3f2g1h$ set of diffuse and core-correlating functions, there still would be a larger number of large and small functions generated by this reduced set than those associated with the respective RPF-4Z one.

3. CONCLUSIONS

The relativistic prolapse-free Gaussian basis sets of quadruple-ζ quality, RPF-4Z, reported here for the d-block elements and presented previously for the s- and p-block ones,[1] are recommended to be used in general atomic and molecular relativistic calculations. Molecular tests addressing fundamental properties attested a quadruple-ζ quality of these sets whereas a significant reduction in CPU demand was achieved in comparison with the dyall.v4z sets. An augmented version,

the aug-RPF-4Z set, which includes one extra diffuse function for each angular symmetry, is also furnished. These are indicated for anionic systems and studies of weak long-range interactions, for example.

The RPF-4Z and aug-RPF-4Z sets can be found in a ready-to-use format in the Supporting Information and at http://basis-sets.iqsc.usp.br/. As soon as possible, we will also provide the (aug-)RPF-4Z sets for the f-block elements in order to complement this series for the entire periodic table.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
RPF-4Z and aug-RPF-4Z sets 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.

■ ACKNOWLEDGMENTS

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