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REGULAR ARTICLE

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Systematic sequences of geometric relativistic basis sets. I:s- and p-Block elements up to Xe

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Abstract In this work a scheme for constructing systematic sequences of relativistic SCF basis sets at a reasonable computational cost is presented and applied to atoms of the s- and p-block up to Xe. This scheme, which couples simplex optimization and the use of geometric series given by four-term polynomial expressions for the logarithm of the exponents, allows for the construction of basis sets that exhibit very regular patterns of convergence to the numerical reference values of atomic total energies, spinor energies and radial expectation values. This regularity, together with the broad range of basis set sizes presented, enables these sets to be used as building blocks for basis sets applicable in both routine and benchmark relativistic calculations on atomic and molecular systems.

Keywords Geometric basis sets · Relativistic basis sets · s-Block elements · p-Block elements · Systematic sequences

1 Introduction

The field of relativistic quantum chemistry has been rapidly evolving over the last three decades, stimulated by advances in computer technology and by the growing interest in heavy element chemistry. In this period there have been many advances in the development of computer codes and theoretical methods [1–3], although the development of basis sets with sizes compatible with use in molecular calculations has not seen corresponding developments until recently, as in the work of Dyall [4–6] (in preparation, available from the Dirac web site, `http://dirac.chem.sdu.dk`), Faegri [7,8] or Tatewaki and coworkers [9–11].

The basis sets available so far, and which have sizes compatible with molecular applications, are of at most quadruple-zeta quality. It is reasonable to assume, from what has been established through cumulative evidence in non-relativistic calculations [12,13], that relativistic basis sets of double and triple zeta quality should be reasonably accurate for most routine calculations, but may not be enough for benchmark calculations of energies and properties that should approach basis set completeness.

It is therefore important to develop basis sets that show systematic improvements in the calculated properties of interest as they are enlarged, not only to allow for a better understanding of the behavior of relativistic basis sets as they approach completeness (as that might be useful in devising extrapolation schemes for energies and properties), but also to have a better idea of the influence of basis set incompleteness errors in calculations involving heavy elements.

Thus, in this work we introduce a procedure suitable for the development of systematic sequences of basis sets, and apply it in the construction of sequences of relativistic SCF basis sets for s- and p-block elements up to Xe. This procedure consists of coupling simplex optimization with geometric series which closely resemble the distribution of fully optimized exponents. The quality of such sequences is evaluated in atomic calculations by inspecting the behavior of the total energies, spinor energies and radial expectation values.

2 Methods

A proven scheme to enlarge basis sets in a systematic way relies on the use of geometric series as generators for the exponents. The systematic procedure pioneered by Ruedenberg and co-workers [14,15] used even-tempered basis sets. Due to the peculiarities of relativistic basis sets, which usually

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require more functions than their non-relativistic counterparts (particularly tight functions) to achieve the same degree of accuracy in atomic energies or other properties, more flexibility than that provided by the use of even-tempered sets is needed in a generator formula, in order to keep the basis set's sizes as small as possible.

We have thus opted to use a generator formula which, while more flexible than the even-tempered expression, still has a relatively small set of parameters to be optimized. This expression is given by the polynomial expression [16] for $\log \zeta_{i,l}$ (where $\zeta_{i,l}$ is the ith exponent of a set with angular momentum l),

$$\log \zeta_{i,l} = p_{0,l} + p_{1,l}(i-1) + p_{2,l}(i-1)^2 + p_{3,l}(i-1)^4, \tag{1}$$

with $i = 1, \ldots, N_l$ and N_l being the number of exponents of a given orbital angular momentum. This formula is closely related to the one proposed by Klobukowski [17,18]

$$\log \zeta_{i,l} = p_{0,l} + p_{1,l}(i-1) + p_{2,l}(i-1)^2 + p_{3,l}(i-1)^3 + p_{4,l}(i-1)^4, \tag{2}$$

but has the advantage of having one less parameter per angular symmetry to be optimized while yielding essentially the same results as the latter.

The parameters $\{p_{k,l}\}$ of Eq. (1) are obtained by minimizing the total atomic energy (for open shell systems the average of configurations energy is used) with the simplex method of Nelder and Mead [19]. In order to enable their use in the molecular programs available to date, we opted to restrict the exponents to be the same for all possible j values for a given orbital quantum number, that is, these sets are l optimized. A gaussian distribution [20] was used to model a finite nucleus in all calculations. The simplex implementation used in our optimizer is a slighlty modified version of the routine given by Press et al. [21] rewritten in the Perl programming language [22]. As the optimizer is not capable of calculating atomic energies the actual ab initio calculations are executed by the atomic code of Matsuoka and Watanabe [23].

During the optimization, a restart procedure which consists of running the optimizer for a relatively small number of steps (usually 500), stopping it and restarting from a slighlty different position in parameter space was used. This was done to avoid ending the optimization after reaching local minima with relatively high energies when compared to the global minimum, even though it is not possible to guarantee that the global minimum was reached, due to the flatness of the potential energy surface. It was found that for the first and second row elements two to three restarts are enough to obtain convergence to three to four significant figures for the parameters and better than $\simeq 10^{-6}$ a.u. for the energy.

We have chosen to construct basis sets of the type "$ns(n-5)p$" for the first and second row elements and "$ns(n-5)p(n-10)d$" for the third and fourth row elements, with "n" being the number of primitives used to define the total size of the basis set. As "n" also coincides with the number of s primitives, hereafter we shall employ the number of these functions to implicitly indicate the size of a given basis set (which can be calculated directly from the formulas above). For the elements B–Ca we obtained basis sets in which "ns" ranges from 10 to 28. For the elements Ga–Sr, "ns" ranges from 16 to 30, while for In–Xe it ranges from 18 to 34.

It should be noted that the fixing of differences in the number of s, p and d primitives is of a purely practical nature, as there would be a very large number of possible size combinations if we were to vary these parameters independently. The sizes chosen, however, were selected on the basis of the analysis of the balance of errors among the different angular symmetries for the first and second row atoms perfomed by Klobukowski [18], in which basis sets of the type "$ns(n-5)p$" or "$ns(n-6)p$" usually were well balanced for small to moderately sized sets, while still providing good energies with respect to the fully optimized sets. While we hope that this balance shall be maintained for the elements considered, we acknowledge that this may not be the case for the heavier elements due to the differences in behavior between inner and valence shells, but investigations along this line are beyond the scope of this work.

3 Results

In order to compare different atoms on an equal footing, the results for total and orbital energies as well as atomic expectation values for the $\mathbf{r}^n (n = -2, \ldots, 4)$ operators are presented here as the error in the basis set representation, that is, as differences between the values calculated using the different basis sets and the reference numerical relativistic HF–SCF values calculated by Dyall and Visscher [24]. Thus, the absolute and relative errors for property P are defined as

$$\Delta P = (P_{\mathrm{B}} - P_{\mathrm{NHF}}) \tag{3}$$

and

$$\Delta_r P = \frac{P_{\mathrm{B}} - P_{\mathrm{NHF}}}{P_{\mathrm{NHF}}}, \tag{4}$$

respectively, where P_{B} is the value of the calculated property in the basis set calculation and P_{NHF} the reference numerical value.

3.1 Total energies

The error in the total energy for a calculation with a given basis set, denoted by ΔE_m (m being the atom of interest), is a commonly used criterion in the assessment of basis set quality, due to the its close connection with the variational nature of most basis set optimization procedures. The behavior for ΔE_m as the basis sets are enlarged is summarized in Figs. 1 and 2 for the p-block elements and in Fig. 3 for the s-block elements, respectively. From these figures one sees a clear and well-behaved improvement for the atomic energies as the basis sets' sizes are increases, which monotonically approach the reference numerical Dirac–Fock values. The

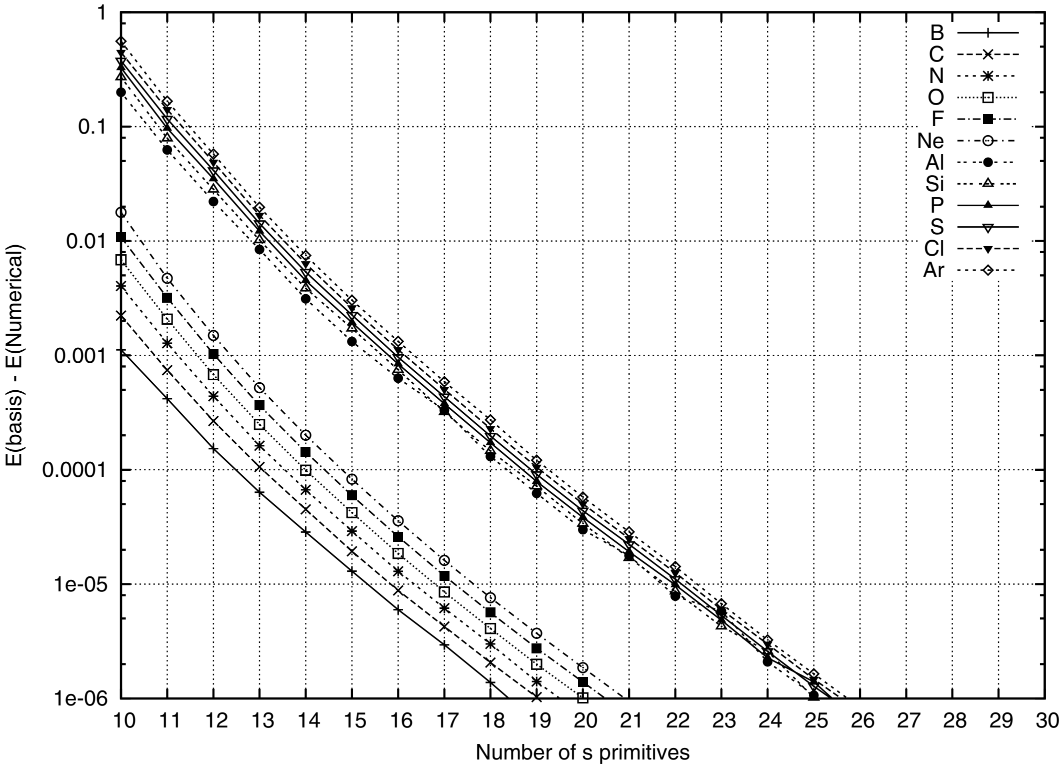

Fig. 1 Deviation of the total energy from the numerical reference values (ΔE_m) with increased basis set size for first and second row p-block elements

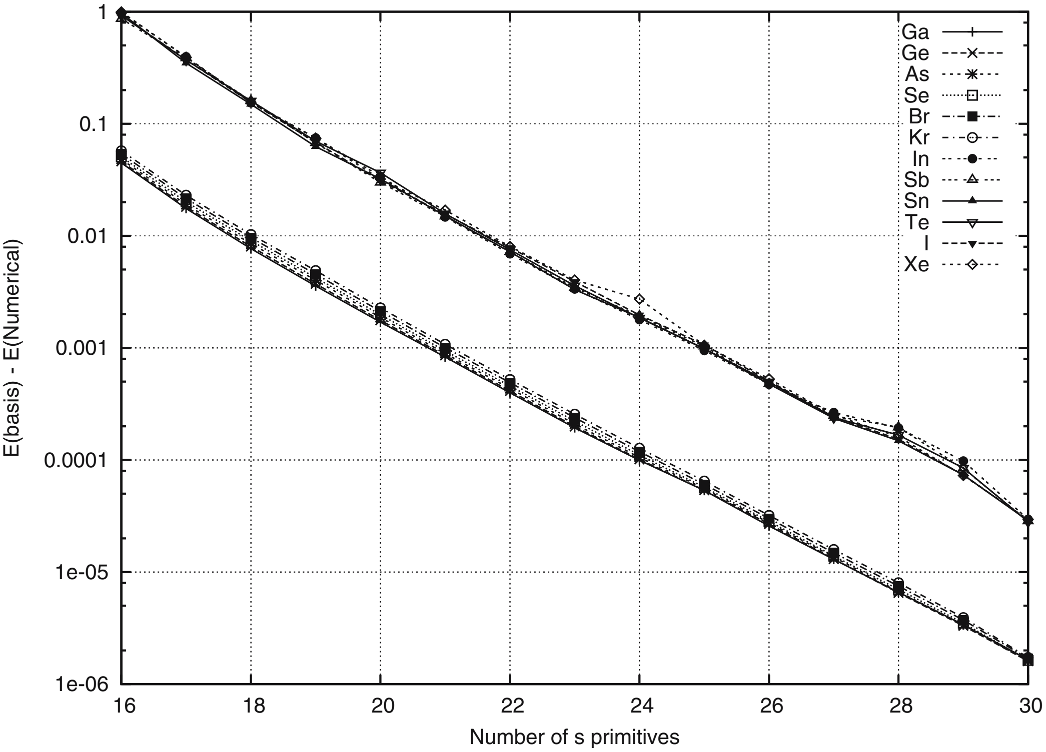

Fig. 2 Deviation of the total energy from the numerical reference values (ΔE_m) with increased basis set size for third and fourth row p-block elements

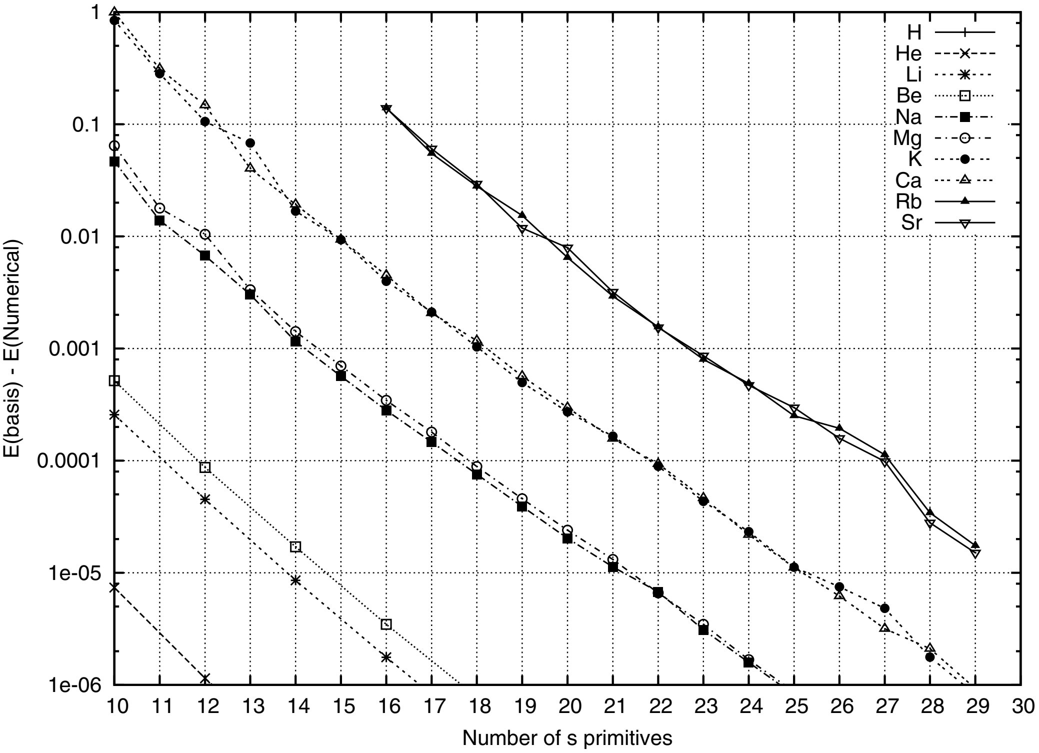

Fig. 3 Deviation of the total energy from the numerical reference values (ΔE_m) with increased basis set size for s-block elements

variations in ΔE_m roughly follow an exponential decrease which means that for smaller basis sets there will be large variations in ΔE.

As a consequence of this exponential behavior, there are regions of relatively small basis sets where large variations on ΔE occur upon enlargement, and regions of moderately sized and large sets for which a slow but steady improvement in the energies is observerd. For the elements considered here, the regions of higher variation of ΔE upon basis set enlargement are seen for sets smaller than about (a) "*ns*" = 12 for the first row, (b) "*ns*" = 16 for the second row, (c) "*ns*" = 21 for the third row and (d) "*ns*" = 25 for the fourth row elements. This behavior reflects the difficulty of a basis set to describe a system as the number of electrons is increased and, as a result, there is a need for describing a much broader region in space than those required for the atoms in the previous row of a given group. In addition, the increasing energy of the deep core levels makes it harder to obtain the same absolute energy convergence as can be achieved for lighter elements.

For larger basis sets, the rate of change in ΔE_m with respect to "*ns*" takes up a constant rate of about two ($\Delta(\Delta E_m)/\Delta(ns) \simeq 2$), with slightly different values for the s and p blocks. This regularity is important as it not only indicates consistency within and among blocks but also hints at a possibly adequate behavior if extrapolations are to be attempted, while being a helpful tool during the optimization. The differences in the ranges where ΔE varies strongly for each row, on the other hand, suggests the need to use basis sets with similar accuracies in ΔE if these are used in molecular calculations, to avoid spurious effects caused by varying degrees of convergence with respect to the SCF limit within the molecule. Another interesting pattern that emerges is that the differences in ΔE's within a given row decreases as one moves down the periodic table. This could be related to the degree of saturation of the basis sets or to the large number of particles to be described, so that the perturbation to the density upon addition of a proton and electron is much weaker than for the same change in lighter atoms.

The basis set sequences appear to be free from the so-called "variational prolapse" [5] at the first inspection, as no energies fall below the numerical reference values. One may, however, verify from the monotonic behavior of the ΔE's obtained here that the conditions proposed by Tatewaki for devising "prolapse-free" basis sets [11,25,26],

$$\delta E(n) = E(n-1) - E(n) > 0, \quad \lim_{n\to \text{large}} \delta E(n) \to 0 \tag{5}$$

$$\Delta E(n) = E(n) - E(\text{NHF}) > 0, \quad \lim_{n\to \text{large}} \Delta E(n) \to 0 \tag{6}$$

n being the size of the expansion, are met even though these conditions were not enforced during the optimization.

3.2 Spinor energies

Although total atomic energies an important measure of basis set quality, they are essentially a global indicator and, as such, miss entirely any local information regarding the wavefunction. In order to deal with this shortcoming we have also

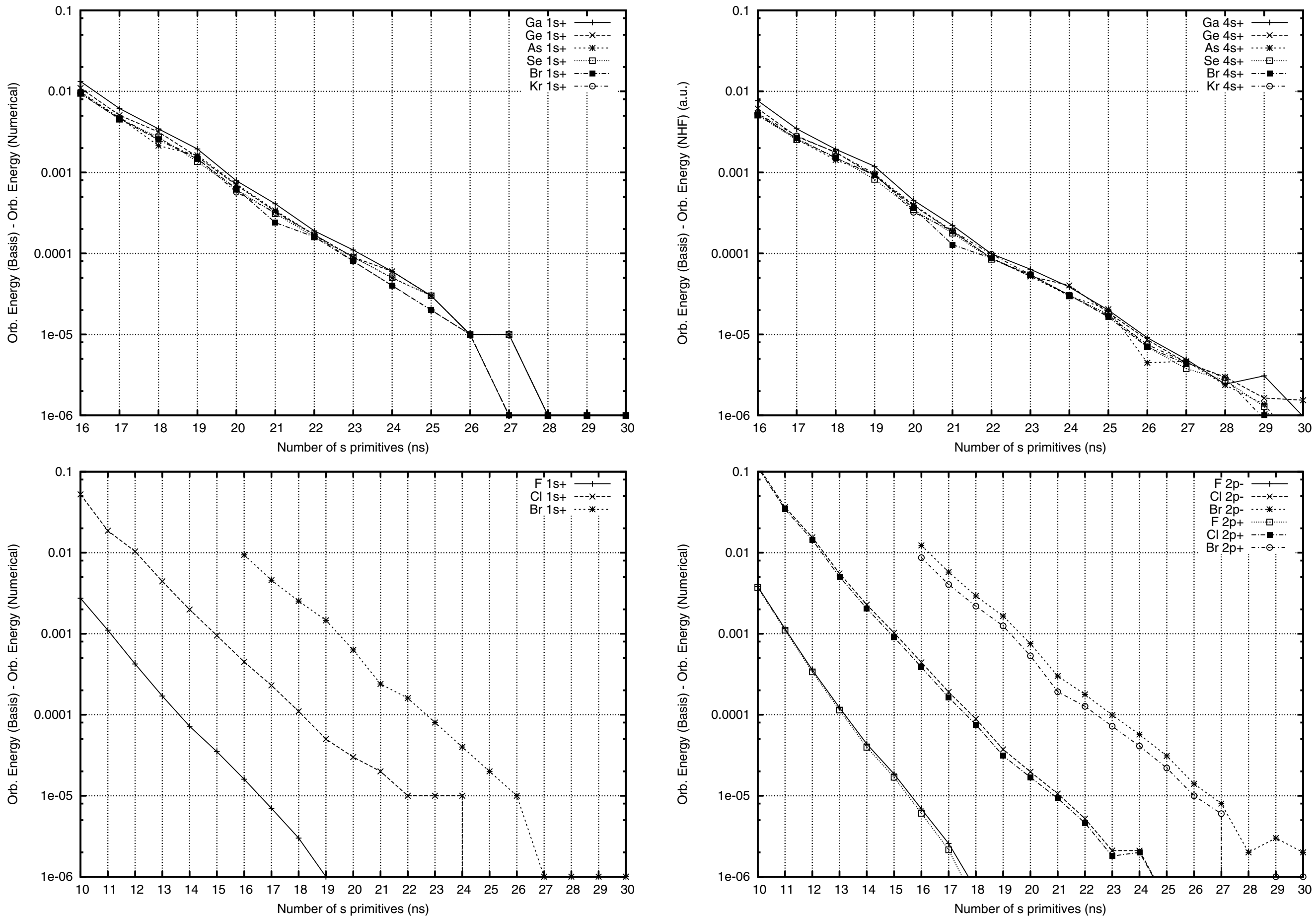

Fig. 4 Absolute $\Delta\epsilon_{mn}$ values for the $1s_{1/2}$ and $4s_{1/2}$ spinors for third row atoms (*top*); and for the $1s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ spinors for the halogen atoms (*bottom*)

analyzed the behavior of spinor energies ϵ_{mn} calculated with different basis sets, as well as the difference among these and the reference values obtained from numerical calculations, expressed by $\Delta\epsilon_{mn}$ (m being the atom and n the spinor of interest). The analysis of the spinor energies for the basis sets obtained in this work has revealed similar behavior to those found for the total energies, that is, large variations for the smaller basis sets, followed by a slow but steady convergence to the reference values as the basis sets are enlarged. To illustrate such behavior we consider the variations within a row (the third row) and within a group (the halogens), shown in Fig. 4.

Considering first the behavior for the $1s_{1/2}$ and $4s_{1/2}$ spinors for the third row (as $2s_{1/2}$ and $3s_{1/2}$ are intermediate cases), it is seen that the $\Delta\epsilon_{mn}$ for different atoms are close to each other, as is the case for ΔE_m. Interestingly, the absolute errors for the core and valence spinors are of the same magnitude. However, as the magnitude of $\epsilon_{k,1s_{1/2}}$ is much larger than that of $\epsilon_{k,4s_{1/2}}$, the relative errors will be much smaller for the former than for the latter. The difference in relative errors is expected, due to the larger weight of the inner orbitals in the calculation of the total energy and, as a result, the optimization procedure ends up providing more accurate inner spinors.

For the halogens, there is a great similarity between the behavior of the absolute errors of ϵ for the $1s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ spinors, in spite of the fact that the differences among $2p_{1/2}$ and $2p_{3/2}$ increase with atomic number. Relative errors show a similar behavior to that observed for the $1s_{1/2}$ and $4s_{1/2}$ spinors for the third row, since $\Delta_r\epsilon_{mn}$ increases as we move towards the valence region . The errors also increase for a given basis set size as we go down the periodic table. But if we compare basis sets that exhibit similar values of ΔE_m (such as $10s5p$ for F, $13s8p$ for Cl and $17s12p7d$ for Br), the behavior of $\Delta\epsilon_{mn}$ follows that of ΔE_m. This supports the previous observation that it might be desirable to group basis sets by similarities in ΔE_m in order to work with sets of approximately the same quality for elements of different rows.

A general feature of the spinor energies for these basis sets is the absence of negative errors, which would occur if the orbital energies were, in absolute value, larger than the reference values. Negative values of $\Delta\epsilon_{mn}$ could be a more sensitive indication for inadequacies in the basis set

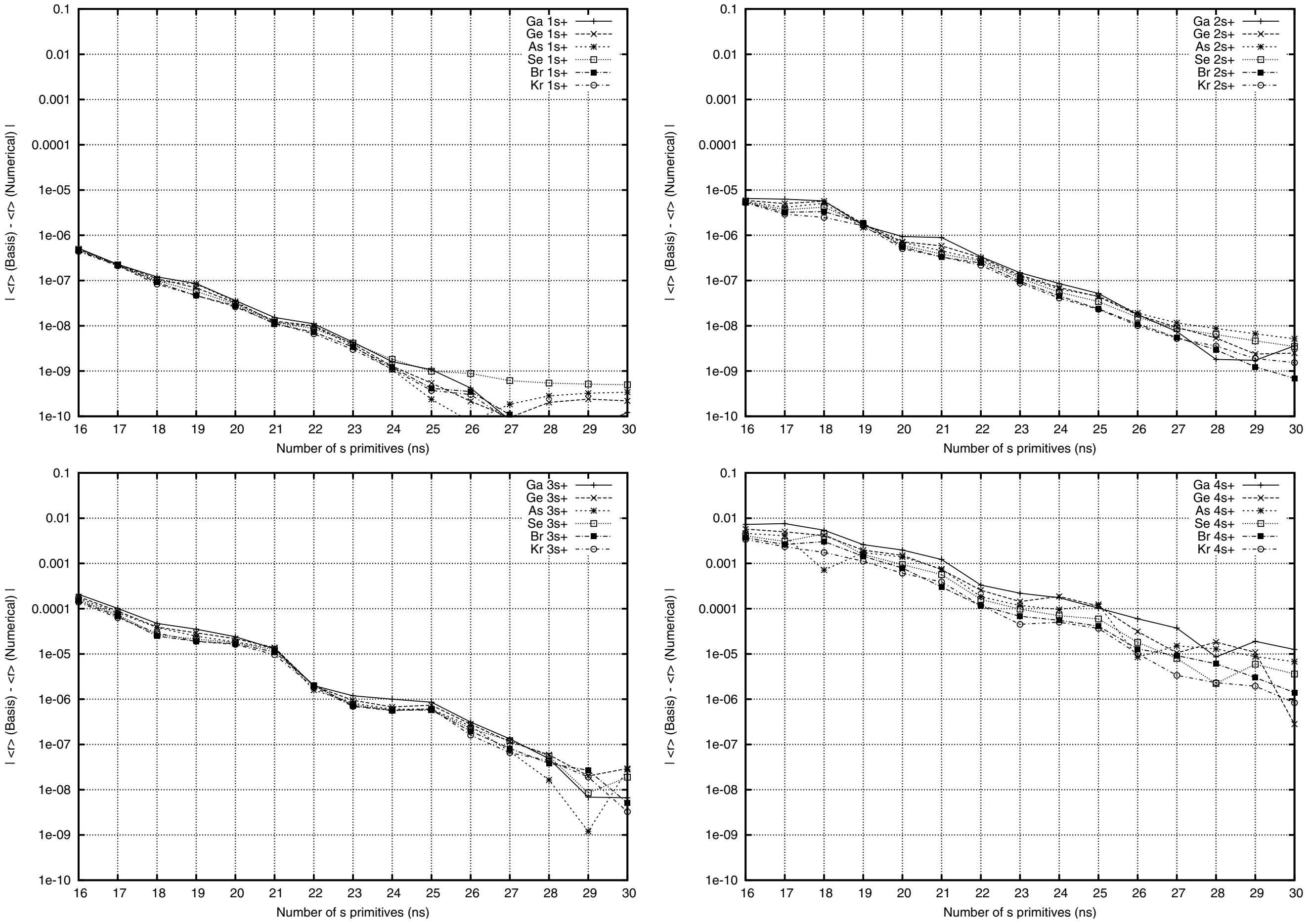

Fig. 5 Values of $|\Delta\langle r\rangle|$ for the $s_{1/2}$ spinors of third row atoms with increased basis set's size

representation for some part of the wavefunction, as they are sometimes seen in the cases of "variational prolapse".

3.3 Expectation values of $\mathbf{r}^n (n = -2, \ldots, 4)$

Complementary to the analysis of energies, the behavior from the expectation values of the $\mathbf{r}^n$ operators is helpful in estimating the local characteristics of the basis sets, but, in this case, with respect to calculated properties. This is because the one-electron property operators will be proportional to the powers of $\mathbf{r}^n$. Thus, here we present the comparison of $\langle\mathbf{r}\rangle$ and $\langle\mathbf{r}^{-1}\rangle$ with their reference numerical values, expressed as $\Delta\langle\mathbf{r}\rangle$ and $\Delta\langle\mathbf{r}^{-1}\rangle$, respectively, for the $ns_{1/2}(n = 1, \ldots, 4)$ spinors of the third row elements as shown in Figs. 5 and 6, respectively.

For $\Delta\langle\mathbf{r}\rangle$ some important differences from the corresponding results for $\Delta\epsilon_{mn}$ are seen, such as the larger oscillations of $\Delta\langle\mathbf{r}\rangle$ as the basis sets are enlarged up to "ns" = 21. In this case, the curves approach the reference values from above for the valence spinor and from below for the others, with $\Delta\langle\mathbf{r}\rangle_{mn}$ increasing as one moves away from the core. It can be seen that the absolute errors increase with atomic number and that, as the basis sets are enlarged, an approximately exponential but slow convergence to the reference values is observed.

These observations for the larger basis sets are also generally valid for $\Delta\langle\mathbf{r}^{-1}\rangle_{mn}$, while for the smaller basis sets there are some distinctive differences. The first is that the variations within the row is even larger than that seen for $\Delta\langle\mathbf{r}\rangle_{mn}$. The behavior of the errors also changes, with convergence to the reference values being less smooth and errors becoming larger than for $\Delta\langle\mathbf{r}\rangle$ as one moves from valence to core spinors. These differences in behavior can be understood if one takes into account the sensitivity of these operators for the different atomic regions: while $\langle\mathbf{r}\rangle_{mn}$ is more sensitive or away from the nucleus, $\langle\mathbf{r}^{-1}\rangle_{mn}$ is closer to it. It is not possible at this time to compare the results from other powers of $\mathbf{r}$ due to the lack of reference numerical values, but from the behavior of ϵ_{mn} these should follow closely what was observed of the operators discussed so far.

It is difficult to establish the reason for the larger variations for properties with increased basis set size. While they may arise from numerical noise, it does not appear likely that linear dependency on the basis sets is a significant factor to it. If one compares the values for the lowest eigenvalues of the

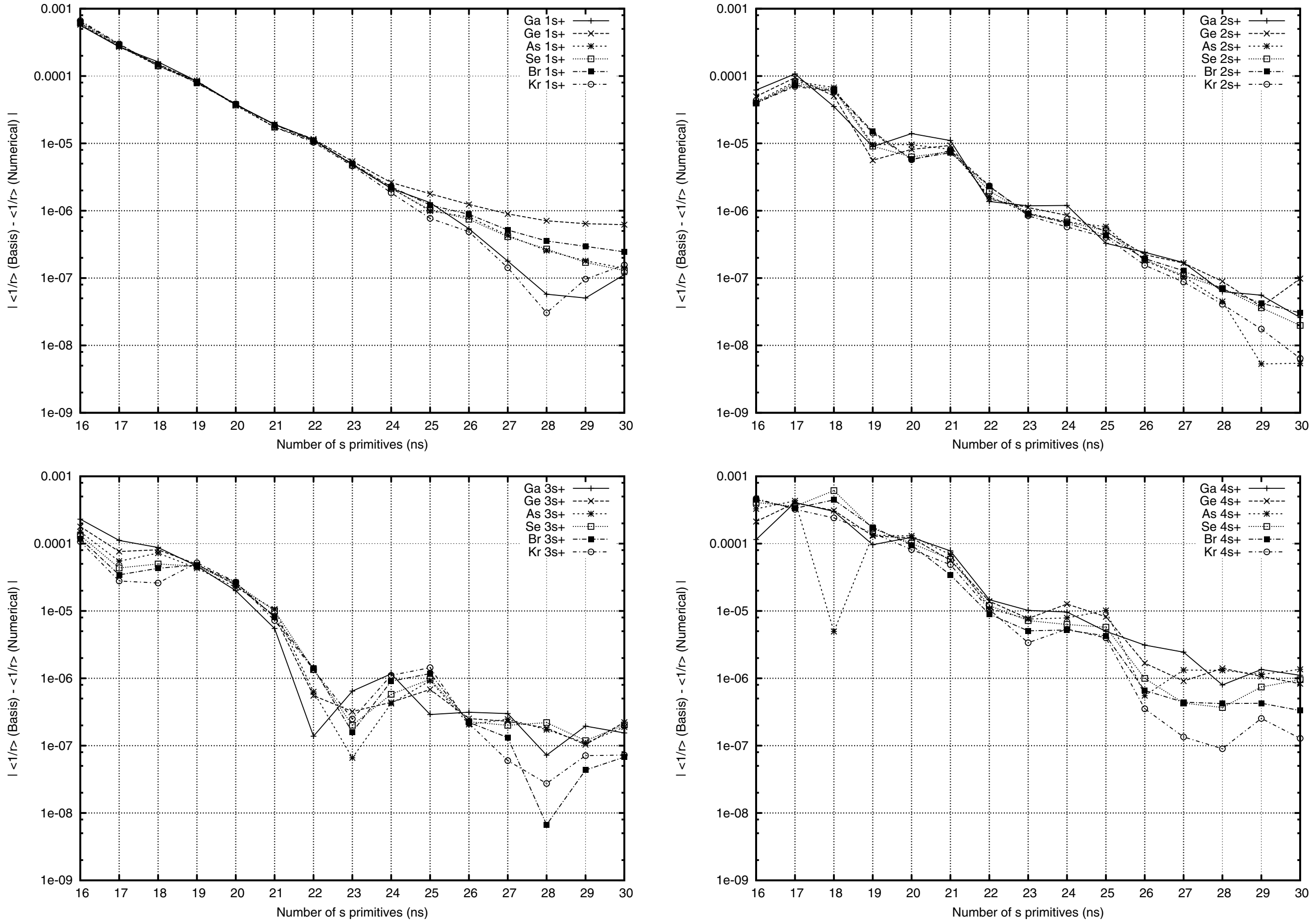

Fig. 6 Values of $|\Delta\langle r^{-1}\rangle|$ for the $s_{1/2}$ spinors of third row atoms with increased basis set's size

overlap matrix for the Br atom, shown in Fig. 7, and the trends for the $\Delta\langle\mathbf{r}\rangle_{mn}$ or $\Delta\langle\mathbf{r^{-1}}\rangle_{mn}$, it is possible to see that variations on the latter appear well before the lowest eigenvalues of S are smaller than 10^{-4}. It could be said, however, that there is some effect of the quasi-linear dependency on the largest sets, as the variations become slightly more pronounced for basis sets with "ns" $>$ 24, for which the eigenvalues of S approach 10^{-5} for the s set.

3.4 Parameters

The systematic behavior seen for the errors in total energies, spinor energies and expectation values is also seen to a good extent in the sets of optimized parameters, provided as supplementary material. It is seen that, as the basis sets approach completeness, the parameters take on values that increasingly resemble an even-tempered expression, due to the decrease of the absolute values of the sets of parameters $p_{2,l}$ and $p_{3,l}$ which represent the deviation from the even-tempered expression.

It is possible to note a similarity in the behavior of parameters for primitives s, p and d, particularly regarding the interval in which these vary. For $p_{1,l}$, the parameters take on values within the range [1.5, 0.6], while for the $p_{2,l}$ this variation is in the range [−0.07, −0.01]. For the $p_{3,l}$ parameters there is a well-defined exponential-like decrease for all angular symmetries, with variations over increasingly smaller values seen when going from s to p as well as from p to d primitives. For $p_{0,l}$, on the other hand, the interval in which s (and p) parameters vary differs considerably from the d exponents; these being [−3, −1] and [−2, 0.25], respectively, indicate a less diffuse behavior for the outer d exponents with respect to the s (and p) meshes.

A higher degree of oscillation can also be seen for the parameter associated with the d exponents than for those associated either with s or p exponents. This might arise from the lesser influence the former have on the total atomic energies and, therefore, their influence in the optimization procedure is diminished with respect to the latter. The oscillations are also seen to increase somewhat with increased atomic number, particularly for $p_{0,l}$.

3.5 Compararison with other relativistic basis sets

For the third row onwards there are some basis sets developed that have been explicitly optimized to take relativistic effects

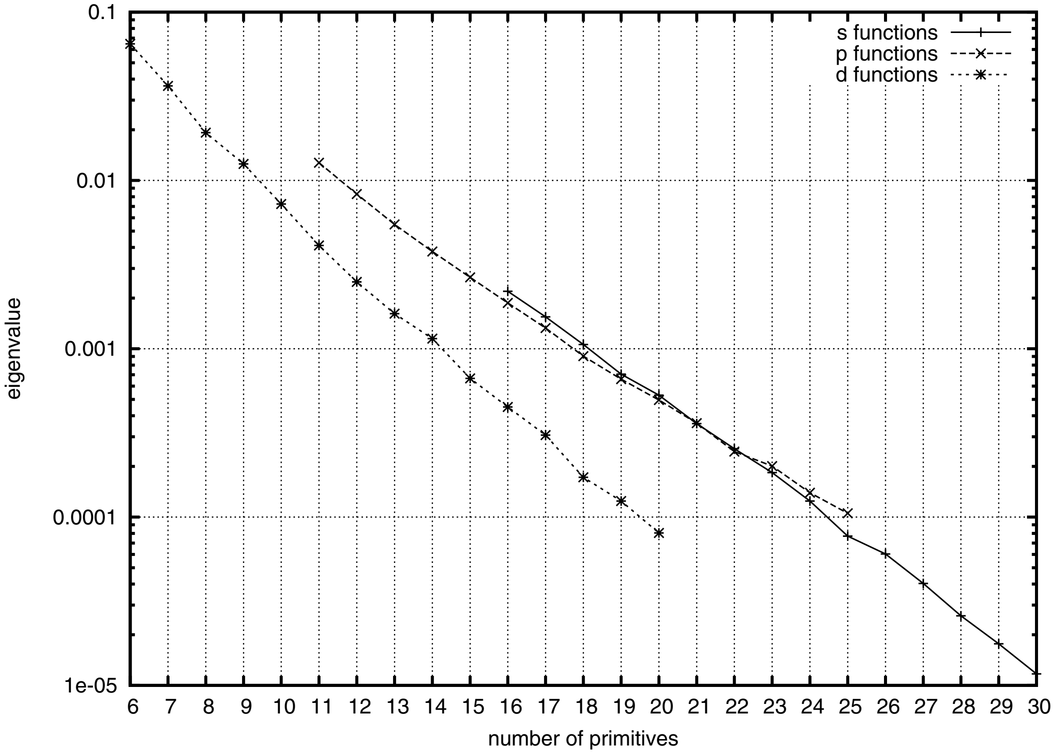

Fig. 7 Lowest eigenvalues of the overlap matrix with increased basis set size for the s, p and d primitive sets of the Br atom

Table 1 Energy differences for the Dyall [4] DZ sets, as well as for similarly sized basis sets from this work; The ΔE values are expressed in mhartrees

Atom	Dyall [4] DZ	ΔE_{DZ}	This work (1)	ΔE_1
Ga	$15s11p6d$	39.593	$16s11p6d$	44.810
Ge	$15s11p6d$	41.039	$16s11p6d$	46.190
As	$15s11p6d$	43.318	$16s11p6d$	48.225
Se	$15s11p6d$	46.256	$16s11p6d$	50.754
Br	$15s11p6d$	49.848	$16s11p6d$	53.825
Kr	$15s11p6d$	53.933	$16s11p6d$	57.341
In	$19s15p9d$	28.654	$19s14p9d$	74.782
Sn	$19s15p9d$	28.916	$19s14p9d$	62.548
Sb	$19s15p9d$	29.678	$19s14p9d$	67.519
Te	$19s15p9d$	30.734	$19s14p9d$	69.943
I	$19s15p9d$	32.245	$19s14p9d$	68.344
Xe	$19s15p9d$	33.952	$19s14p9d$	74.660

Table 2 Energy differences for the Dyall [5] TZ sets, as well as for similarly sized basis sets from this work; the ΔE values are expressed in mhartrees

Atom	Dyall [4] TZ	ΔE_{TZ}	This work (2)	ΔE_2
Ga	$23s16p9d$	0.650	$22s17p12d$	0.397
Ge	$23s16p9d$	0.666	$22s17p12d$	0.413
As	$23s16p9d$	0.700	$22s17p12d$	0.435
Se	$23s16p9d$	0.748	$22s17p12d$	0.458
Br	$23s16p9d$	0.807	$22s17p12d$	0.490
Kr	$23s16p9d$	0.873	$22s17p12d$	0.523
In	$28s21p14d$	0.294	$27s22p17d$	0.265
Sn	$28s21p14d$	0.306	$27s22p17d$	0.235
Sb	$28s21p14d$	0.322	$27s22p17d$	0.248
Te	$28s21p14d$	0.342	$27s22p17d$	0.238
I	$28s21p14d$	0.365	$27s22p17d$	0.242
Xe	$28s21p14d$	0.391	$27s22p17d$	0.251

into account, so a comparison of the sets developed here to those is also helpful in evaluating the results obtained so far.

In Tables 1 and 2 are shown, respectively, a comparison of some specific basis sets developed here and those of double [4] and triple-zeta [5] quality developed by Dyall via a complete optimization of exponents by gradient methods. While it is difficult to compare the sets as the sizes vary greatly, it is clearly seen that Dyall's basis sets generally exhibit better results than those obtained by geometric series as expected, due to the greater variational flexibility warranted by the unconstrained optimization. Another difference between Dyall's results and those from this work is that in the latter the differences in ΔE_m across the rows are smaller. In spite of this, it is interesting to note that the difference in absolute terms is usually not very large, while in relative terms it reaches at most a factor of 2 for the comparison with fourth row DZ sets. As these sets are in a region where the changes in energy with respect to basis set size are very pro-

Table 3 Comparison of energy differences (ΔE) for the Fægri [7] DZ sets and of similarly sized basis sets from this work; the ΔE are in mhartrees

	Basis set (Ref. [7])	ΔE_m (Ref. [7])	Basis set (this work)	ΔE_m (this work)
K	$19s14p$	0.3	$19s14p$	0.5
Ca	$19s14p$	0.3	$19s14p$	0.6
Ga	$19s16p9d$	2.8	$19s14p9d$	3.6
Ge	$19s16p9d$	2.8	$19s14p9d$	3.7
As	$19s16p9d$	2.8	$19s14p9d$	4.0
Se	$19s16p9d$	2.8	$19s14p9d$	4.2
Br	$19s16p9d$	2.8	$19s14p9d$	4.5
Kr	$19s16p9d$	3.0	$19s14p9d$	4.9
Rb	$20s16p9d$	3.8	$20s15p10d$	6.5
Sr	$20s16p9d$	3.7	$20s15p10d$	7.9
In	$20s18p11d$	9.5	$21s16p11d$	14.8
Sn	$20s18p11d$	9.6	$21s16p11d$	15.0
Sb	$20s18p11d$	9.8	$21s16p11d$	15.0
Te	$20s18p11d$	9.9	21s11p11d	15.7
I	$20s18p11d$	10.0	$21s16p11d$	15.7
Xe	$20s18p11d$	10.2	$21s16p11d$	16.9

nounced, a small difference in size can yield significantly different energies.

A second comparison with fully optimized basis sets is shown in Table 3, where the double-zeta "family-type" basis sets of Fægri [7] are compared to similarly sized basis sets (a peculiarity of the "family-type" scheme is that $s, d, g, \ldots$ and $p, f, h, \ldots$ exponents are shared, so it is less flexible in the variational sense than, for example, Dyall's basis sets). For K and Ca, which do not possess occupied d orbital, the comparison of results is straightforward as we may compare the sets of same size. In this case, we see slightly better results for the Fægri sets, with differences of about 0.2–0.3 mhartree among the sets, corresponding to factors of 1.6–2 in relative terms. This difference can again be attributed to the greater flexibility of the individual optimization of the exponents. For the other elements, the comparison is somewhat difficult due to the different basis set sizes considered, but differences in absolute terms of a few mhartrees are observed. The relative differences, on the other hand, tend to decrease to factors ranging from 1.3 to 1.6. This decrease possibly arises from the loss in variational freedom imposed by the "family-type" constraints.

At last, in Table 4 the results from fully j–optimized sets of Matsuoka and coworkers [9] are compared to similarly sized basis sets from this work. It should be noted that the comparison here is complicated by the fact that there is much more variational freedom in Matsuoka's sets than in those presented here, due to the distinct basis sets for the $j = l + 1/2$ and $j = l - 1/2$ functions for $l > 0$. This increased freedom will be more felt the heavier the elements get. In spite of these differences, it can be seen that the results from this work are in good agreement with Matsuoka's, particularly for the lighter elements, where the difference of spinor with $j = l + 1/2$ and $j = l - 1/2$ is rather small. The differences start to increase for the heavier elements, being the largest for Xe. Up to the third row atoms, however, the differences between Matsuoka's results and those presented here are roughly in line with those previously discussed, with ΔE_m values being larger than the j-optimized sets by factors of 1.3–1.5.

3.6 Comparison with polynomial expansions in legendre polynomials

Petersson and coworkers [27] have recently discussed in detail an alternative to polynomial expansions of $\ln \zeta$ used in this work. This alternative, in which monomials such as $\{(i-1)^n\}$ in Eq. 1 are replaced by Legendre polynomials of the appropriate order, was shown to be more robust, particularly when the terms in the expansion is increased. It is thus of relevance to examine how the approach taken here fares when compared to the expansion in Legendre polynomials.

The comparison is seen in Table 5 where values for ΔE for the noble gases taken from the six-parameter expansion of Petersson are shown beside values of ΔE for basis sets developed here, which approximately match those of the former. It should be stressed that, as relativistic and non-relativistic ΔE's are being compared, discrepancies between results will be due to the differences in the expansion of $\ln \zeta$ as well as due to the different basis set sizes required to achieve the same accuracy in both cases.

A comparison of ΔE's shows that, for light elements (He, Ne, Ar), where the differences between the relativistic and non-relativistic basis sets are small, the errors in the total energies are quite similar for basis of approximately the same size. The use of six optimizing parameters in Petersson's formula apparently does not bring about the same improvements with respect to Eq. (1) as those seen when going from an even-tempered set to Eq. (1) in non-relativistic calculations for the

Table 4 Comparison of energy differences (ΔE) for the j-optimized sets of Matsuoka [9] and some similarly sized l-optimized basis sets from this work; the ΔE are in mhartrees

	Basis set (Ref. [9])	ΔE_m (Ref. [9])	Basis set (this work)	ΔE_m (this work)
Li	$12s$	0.032	$12s$	0.045
Be	$12s$	0.057	$12s$	0.087
B	$12s8p$	0.098	$12s7p$	0.153
C	$12s8p$	0.159	$12s7p$	0.267
N	$12s8p$	0.245	$12s7p$	0.440
O	$12s8p$	0.362	$12s7p$	0.678
F	$12s8p$	0.517	$12s7p$	1.027
Ne	$12s8p$	0.718	$12s7p$	1.490
Na	$16s8p$	0.394	$16s11p$	0.281
Mg	$16s8p$	0.489	$16s11p$	0.345
Al	$16s11p$	0.448	$16s11p$	0.632
Si	$16s11p$	0.535	$16s11p$	0.746
P	$16s11p$	0.644	$16s11p$	0.841
S	$16s11p$	0.775	$16s11p$	0.963
Cl	$16s11p$	0.921	$16s11p$	1.120
Ar	$16s11p$	1.081	$16s11p$	1.327
K	$20s11p$	0.693	$18s13p$	1.034
Ca	$20s11p$	0.742	$18s13p$	1.176
Ga	$20s15p9d$	1.190	$20s15p10d$	1.700
Ge	$20s15p9d$	1.248	$20s15p10d$	1.766
As	$20s15p9d$	1.328	$20s15p10d$	1.872
Se	$20s15p9d$	1.425	$20s15p10d$	1.981
Br	$20s15p9d$	1.537	$20s15p10d$	2.123
Kr	$20s15p9d$	1.620	$20s15p10d$	2.279
Rb	$22s15p9d$	1.519	$22s17p12d$	1.559
Sr	$22s15p9d$	1.480	$22s17p12d$	1.537
In	$22s18p12d$	1.936	$22s17p12d$	6.917
Sn	$22s18p12d$	2.304	$22s17p12d$	7.203
Sb	$22s18p12d$	2.159	$22s17p12d$	7.201
Te	$22s18p12d$	2.265	$22s17p12d$	7.524
I	$22s18p12d$	2.367	$22s17p12d$	7.843
Xe	$22s18p12d$	2.456	$22s17p12d$	8.050

same elements [16]. Another important result is that the rate of convergence of the SCF energy as the basis set is increased is roughly the same for both approaches.

For heavier elements, there are larger discrepancies between the two approaches, with Petersson's approach apparently faring better, even though both are still quite close to each other. It is not easy at this point to attribute this difference to the better suitability of Petersson's approach, particularly due to the use of polynomials of higher order than those used here, or to an artifact caused by the comparison of relativistic and non-relativistic results. It would therefore be of interest to investigate Petersson's approach for heavier main-block elements (Tl-Ra), but this is beyond the scope of this work.

4 Conclusions

In this paper we have presented a procedure suitable for generating sequences of basis sets which show systematic convergence to the numerical total atomic energies, spinor energies and radial expectation values for the position operators ($\mathbf{r^n}$, $n = -2, \ldots, 4$). It was found that the improvement of these properties with increased basis set size follows an exponential-like behavior, and that by grouping sets with similar values for the error in the total atomic energy, ΔE_m, it is possible to obtain a group of sets which show approximately the same rate of convergence for all elements considered.

Our results indicate that the use of simplex optimization and expressions such as the four-parameter generator formula of Eq. (1) is an alternative to fully optimizing exponents for relativistic basis sets (particularly for medium and large sets). This conclusion is supported by (i) the relative ease with which relatively large sequences of basis sets can be generated; and (ii) the fact that the errors on the total energies so far have the same order of magnitude as those of fully optimized sets similar in size, but developed employing less constraints in the optimization procedure.

Table 5 Values of ΔE (in mhartrees) for the non-relativistic basis sets of Petersson [27] and for selected basis sets developed here

Atom	Basis	ΔE Ref. [27]	Basis^{a}	ΔE^{a}	Basis^{b}	ΔE^{b}
He	5*s*	1.785	4*s*	6.526	6*s*	0.532
	7*s*	0.166	6*s*	0.532	8*s*	0.057
	9*s*	0.019	8*s*	0.057	10*s*	0.007
	11*s*	0.003	10*s*	0.007	12*s*	0.001
	13*s*	0.0004	12*s*	0.001	14*s*	0.0002
Ne	10*s*6*p*	6.173	10*s*5*p*	17.816	11s6p	4.715
	12*s*8*p*	0.724	12*s*7*p*	1.491	13s8p	0.521
	14*s*10*p*	0.113	14*s*9*p*	0.020	15s10p	0.083
	16*s*12*p*	0.020	16*s*11*p*	0.036	17s12p	0.016
	18*s*14*p*	0.004	18*s*13*p*	0.008	19s14p	0.004
Ar	16*s*10*p*	21.187	15*s*10*p*	57.517	16*s*11*p*	19.732
	18*s*12*p*	2.975	17*s*12*p*	7.462	18*s*13*p*	3.039
	20*s*14*p*	0.530	19*s*14*p*	1.328	20*s*15*p*	0.588
	22*s*16*p*	0.100	21*s*16*p*	0.273	22*s*17*p*	0.121
	24*s*18*p*	0.023	23*s*18*p*	0.058	24*s*19*p*	0.029
Kr	15*s*11*p*6*d*	39.728	16*s*11*p*6*d*	57.341	—	—
	18*s*13*p*8*d*	4.431	18*s*13*p*8*d*	10.293	—	—
	21*s*15*p*10*d*	0.589	20*s*15*p*10*d*	2.279	21*s*16*p*11*d*	1.076
	24*s*17*p*12*d*	0.092	22*s*17*p*12*d*	0.523	24*s*19*p*14*d*	0.127
	27*s*19*p*14*d*	0.015	24*s*19*p*14*d*	0.127	27*s*22*p*17*d*	0.016
Xe	18*s*13*p*8*d*	59.517	18*s*13*p*8*d*	156.061	—	—
	21*s*15*p*10*d*	7.317	20*s*15*p*10*d*	32.151	21*s*16*p*11*d*	16.991
	24*s*17*p*12*d*	1.111	22*s*17*p*12*d*	8.051	24*s*19*p*14*d*	2.721
	27*s*19*p*14*d*	0.178	24*s*19*p*14*d*	2.721	27*s*22*p*17*d*	0.252
	30*s*23*p*18*d*	0.037	26*s*21*p*16*d*	0.530	30*s*25*p*20*d*	0.029

[a] Smaller than or equal to those presented in [27]
[b] Larger than those presented in [27]

Due to the different basis set sizes which make up these sequences, their relative closeness to the results of fully optimized basis sets, as well as to the systematic patters observed for the properties above, it is expected that these can be applied, when supplemented with suitable polarization functions, from routine to highly accurate calculations in molecular systems.

However, if additional economy in the number of primitives is required while maintaining a given degree of accuracy in the total energies, as could be the case for the smaller and intermediately sized basis sets, the sequences developed here could quite possibly be used as the starting point in developing sequences of fully optimized sets at a substantially lower computational cost than starting from scratch, as these exponents should be reasonably close to the fully optimized ones.

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