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# Relativistic Gaussian basis sets for the elements K – Uuo

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**Abstract.** A series of energy-minimized relativistic Gaussian basis sets for the elements with atomic numbers 19–118 is presented. The basis sets have been derived at the self-consistent field level as weighted average energies of the respective electronic configurations. A spherical Gaussian charge distribution has been used to model the nucleus. The basis sets are constructed as interleaving dual family sets with shared exponents within each family. The quality of the basis sets is better than double zeta.

**Key words:** Gaussian basis sets – Relativistic basis sets – Dirac–Hartree–Fock – Basis set optimization

## 1 Introduction

For some time there has been growing awareness of the importance of relativistic effects on bonding in molecules as well as other molecular properties. This has spurred efforts to extend the methods of computational quantum chemistry to provide a quantitative description of relativistic effects in molecules. The development of such relativistic methods has followed several different theoretical models, among these the use of relativistic effective core potentials, Foldy–Wouthuysen or Douglas–Kroll methods, perturbation theory, and four-component methods. The most demanding of these in terms of computational effort are the four-component methods, but it is also these approaches which involve a minimum of approximations to the relativistic theory developed by Dirac. Thus, there has for some time been a steady development of computer programs for four-component relativistic calculations on general polyatomic systems.

Like most nonrelativistic computer programs for general polyatomic molecules, these molecular four-component programs are based on an analytic approximation using expansion of the wavefunction in basis sets of Gaussian functions. One obstacle to the application of four-component methods has been the rather limited availability of basis sets for these types of calculations. Various basis sets have appeared, including the universal Gaussian basis (UGB) sets [1, 2, 3], least-squares fitting to a numerical wavefunction [4], even-tempered expansions [5, 6], modified nonrelativistic sets [7, 8], and energy-minimized sets [9, 1]. Most of these sets are either derived for special applications to specific elements or at most cover only a limited range of elements. An exception is the UGB, but while this set yields results of high accuracy in atomic calculations, it appears rather large for use in routine calculations on molecules.

The purpose of the present work is to provide basis sets for routine work in four-component calculations on molecules. The goal has been to derive a series of basis sets spanning a wide range of elements with reasonably uniform quality and at the same time of a size compatible with use on present-day average-sized computational resources. The method and the strategies chosen in deriving these basis sets are described later. This is followed by a section containing comments on the results and a discussion of some features of the basis sets and on the procedure used.

## 2 Method

The basic idea behind the development of the present basis sets is simple. To describe the radial part of an atomic spinor we seek a set of Gaussian functions of the type

$$x^p y^q z^r e^{-\zeta r^2} \ , \qquad (1)$$

where the exponents, $\zeta$, are chosen such that the basis set provides a best possible description of the atom, compatible with its use in molecular calculations. As a quality criterion the minimization of the total atomic energy calculated with the basis set is used, in accordance with the variational principle. For this purpose a modified version of the GRASP [11] program package

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has been interfaced to optimization routines that search for a minimum on the energy hypersurface spanned by the exponents for the Gaussian functions of the basis set. The method and the technical implementation has been described in previous articles [9, 10].

In deriving a basis set along these lines, a number of strategic decisions must be made. A general discussion of the possible choices is presented in Ref. [9]; only those pertaining to the present work will be considered here. One such decision is how to group the functions in the basis set. For nonrelativistic basis sets, the functions are normally grouped according to angular momentum quantum number, $\ell$, into $\ell$-based sets. The symmetry of a relativistic atomic spinor is characterized by the value of the quantum number $\kappa$; thus, to provide maximum variational freedom, one might want to optimize subsets for each value of $\kappa$ to provide a $\kappa$-based set. The use of $\kappa$-based sets would unfortunately lead to basis sets that are too large for most practical applications and is, therefore, not a viable option here. Another possibility is to group the functions into $j$-based sets, where the subsets have the same value of the quantum number $j$. There are a number of good arguments for using $j$-based sets, but in order to exploit these efficiently, the relativistic molecular program must use two-spinor based algorithms, as opposed to algorithms based on the scalar components of the four-spinor. Not all programs available today have this possibility. Furthermore, for the lighter elements it is clearly sensible to have the same functions for, say, $p_{1/2}$ and $p_{3/2}$. For these reasons, it has been decided to work with $\ell$-based sets. This also has the advantage that it is easy to make the connection to the nonrelativistic case and the sets may be modified for use in more approximate schemes if so desired.

The basis sets for the large component and the small component of a four-spinor must be related by the requirement of kinetic balance, approximately expressed as

$$\{\psi^{\mathrm{S}}\} \supseteq \{(\sigma \cdot \mathbf{P})\psi^{\mathrm{L}}\} \ , \tag{2}$$

In practice this is fulfilled by letting the small-component basis consist of the derivatives of the basis functions of the large components. Thus, in $\ell$-based sets, the large-component s functions generate small-component p functions, large p functions generate small s functions and small d functions, large d functions generate small p functions and d functions etc. Therefore, the number of small-component functions may become rather large owing to the kinetic balance requirement. One remedy for this is to use family sets, where large-component basis functions that generate the same type of small components also having coinciding exponents. In this scheme, the exponents for the d functions would be a subset of the s function exponents and any possible g functions would also have exponents from this set. The other (interleaving) family would consist of p, f, and h functions. Sets constructed in this manner have previously been given the name dual family sets, and the present series of basis sets have been chosen on this model. In practice it turns out that the internal restrictions on a dual family set require that more basis functions be used for the larger $\ell$ values to reach the same atomic energy as a nonfamily (or bachelor) set, and this offsets some of the savings in the small-component function space. However, the dual family set has the additional advantage of reducing the danger of linear dependencies in the small-component space, something which may be a problem for large bachelor sets. It should be recalled that for Cartesian Gaussian functions the "extra functions" for the higher $\ell$-values also have to be included in the small-component space, i.e. the 3s function generated by Cartesian d functions and the 4p functions form the f functions; this increases the possibilities for linear dependencies. The increased possibilities for linear basis set dependencies are due to the approximate form of the kinetic balance used in four-component molecular calculations and the use of $\ell$-based sets. Thus, the small components for $s_{1/2}$ and $d_{3/2}$ both appear as p functions rather than $p_{1/2}$ and $p_{3/2}$, respectively.

The size of basis sets chosen arises as a compromise between maximum flexibility and minimum cost. The experience from nonrelativistic calculations is that basis sets of at least double-zeta quality (i.e. at least two primitive functions describing the valence spinors) are required to provide reasonable results at the Hartree–Fock level and that sets beyond this, augmented by various polarization functions, are required for more accurate work. The present sets have been chosen to be of double-zeta to triple-zeta quality. For relativistic basis sets some special considerations apply. One such special demand arises out of the spin-orbit splitting. With $\ell$-based sets, the same exponents have to describe components of both $j$ values. For light elements, this may not be critical but for heavy atoms this may create more of a strain, and in the worst case one of the two $j$ components may end up with a poorer description.

Because the relativistic energy lowering is greatest for the $s_{1/2}$ and $p_{1/2}$ spinors, an energy-minimization procedure is likely to overemphasize the inner regions of the s spinors. Therefore trying to achieve a natural triple-zeta distribution for s spinors may require an inordinately large number of basis functions in regions that are energetically important, but less essential for a description of the valence region, which decides much of the chemistry. The same may apply to p spinors for heavier elements. This may have consequences for the energy balance of the basis set. A basis set is said to be energy-balanced if the addition of one more function, followed by reoptimization, produces the same energy improvement for all $\ell$ values. With the large energy contributions from the low-$\ell$ symmetries, it may be permissible to forego some of the energy balance for these.

The use of a finite nuclear size is important for relativistic basis sets. For a point nucleus, there will be spinors that are singular at the nucleus, and the minimization process tries to model this singularity at great expense of a number of high exponent basis functions. The use of a finite nuclear model removes the singularity and also reduces some of the energy contribution to the spinors with the greatest penetration to the nuclear region. For these calculations we chose a Gaussian nuclear charge distribution in accordance with the prescription by Visscher and Dyall [12]. In this model the atomic mass of the element determines the exponent of the

Gaussian charge distribution. The particular isotope (or average) mass chosen for this is not critical for the basis set, but it does affect the value of the total energies; thus, one should not expect to reproduce these with a different atomic mass number.

The basis sets presented here cover the atomic numbers 19–118. For elements lighter than this, there is a wide selection of nonrelativistic basis sets which may be used in relativistic calculations with insignificant loss of accuracy, provided proper attention is paid to the modification of any contractions used. The basis sets were optimized in average-level Dirac–Fock calculations, and for most cases the standard ground-state electronic configuration was used.

## 3 Results

The overall features of the present series of basis sets are presented in Table 1. A more comprehensive listing including total energies is provided in the Appendix. The full listing of the basis set exponents is available from the Internet archives. This listing also contains the spinor coefficients, which may be of use, for example, in contracting the basis sets. In the following, we comment briefly on some features of the various series of elements. The general notation used for a family basis is of the form ($n_s$, $n_p$, $n_d$: $m_s$, $n_f$: $m_p$), meaning for $n_\ell$ functions are used for this value $\ell$, and $m_\ell$ is the lowest common exponent in the family set. Thus a (25, 23, 17:8, 12:10) set has 25 s functions, 23 p functions, 17 d functions with the same exponents as s functions number 8 to 24 (ordered by decreasing magnitude), and 12 f functions sharing exponents with p functions number 10 to 21.

### *K–Ca: (19, 14)*

The concept of family sets does, of course, not apply to these elements which only contain s and p spinors. Although the exponents here are derived from a scaled Sc set, with triple-zeta s distribution, the inner functions slide towards higher exponents, leaving a double-zeta set. The p distribution is quadruple zeta, which is larger than what is aimed at with these sets, but not of great consequence, as these are really light elements in the context of relativistic calculations, and if the relativistic effects on these elements are of primary interest, in a calculation, an extensive basis will be required.

**Table 1.** Overview of basis set series. $\Delta E$ is the deviation from the numerical value in m$E_H$

| Atoms | Basis set | $\Delta E$ |
|---|---|---|
| K–Ca | (19, 14) | 0.3 |
| Sc–Zn | (19, 14, 9:9) | 0.9–3.0 |
| Ga–Kr | (19, 16, 9:9) | 2.8–3.0 |
| Rb–Sr | (20, 16, 9:9) | 3.8–3.7 |
| Y–Cd | (20, 16, 11:9) | 5.3–9.7 |
| In–Xe | (20, 18, 11:9) | 9.5–10.2 |
| Cs–Ba | (23, 19, 12:9) | 4.3–4.2 |
| La | (23, 19, 14:9) | 5.1 |
| Ce–Lu | (23, 19, 14:9, 9:10) | 6.1–17.9 |
| Hf–Hg | (23, 19, 14:9, 9:10) | 17.3–18.8 |
| Tl–Rn | (23, 21, 14:9, 9:10) | 17.6–18.5 |
| Fr–Ra | (25, 21, 14:9, 9:10) | 17.4–17.0 |
| Ac | (25, 21, 16:9, 9:10) | 17.8 |
| Th–Lr | (25, 21, 16:9, 12:10) | 19.8–34.9 |
| Rf–112 | (25, 21, 17:8, 12:10) | 29.1–29.5 |
| 113–118 | (25, 23, 17:8, 12:10) | 20.6–16.3 |

### *Sc–Zn: (19, 14, 9:9)*

For the first row of transition elements, we now obtain a triple-zeta s distribution. The p functions still make a quadruple-zeta set. A reasonably regular increase of the deviation from the numerical value appears as we go to higher atomic numbers, in agreement with what is observed for most energy-optimized basis sets. The $s^2 d^n$ configuration was used, except for Cr and Ni where the $s^1d^{n+1}$ configuration is preferred.

### *Ga–Kr: (19, 16, 9:9)*

Adding two functions to the p space provides a triple-zeta distribution. Also the s distribution is triple zeta in the valence, but this is at some cost to the description of the 3s spinor, which has shrunk to double zeta by the time we get to Kr.

### *Rb–Sr: (20, 16, 9:9)*

From here on, we settle for double-zeta s distributions for reasons discussed in the previous section. We still maintain a triple-zeta p distribution.

### *Y–Cd: (20, 16, 11:9)*

The second row of transition metal elements continues the s double-zeta and p triple-zeta distributions from Rb. The d distribution starts out as triple zeta, but is closer to quadruple zeta by the time we reach Cd. The $s^1d^{n+1}$ configuration was used for Mo and Pd, otherwise $s^2d^n$ was used.

### *In–Xe: (20, 18, 11:9)*

Here two p functions have been added. This is not enough to support a triple-zeta p description for In and Sn, owing to the small contribution to the total energy from high-lying valence spinors with only one or two electrons. From Sb onwards, the p distribution is triple zeta.

### *Cs–Ba: (23, 19, 12:9)*

Three s functions, as well as a p and a d function, were added. This is partly to anticipate the increased demands on the p and d distributions as the nuclear charge increases through the lanthanide series. The sets are double zeta for the s functions; triple zeta for p functions, and quadruple zeta for d functions.

*La: (23, 19, 14, 9), Ce–Lu: (23, 19, 14:9, 9:10)*

All the lanthanides were optimized for the $s^2d^1f^n$ configuration. For La the d distribution now becomes triple zeta and this is maintained throughout the lanthanides. It is noteworthy that on going from La to Lu the difference between the finite basis total energies and those obtained from numerical calculations increases monotonically from 5 to 18 m$E_H$. This should be compared to the relatively stable value of this difference from Hf to Ra.

*Hf–Hg: (23, 19, 14:9, 9:10)*

The same distributions apply through the third row of transition metals as for the lanthanides. The $s^1d^{n+1}$ configuration was used for W and Pt, otherwise $s^2d^n$ was used. The effect of spin-orbit splitting is now clearly manifested in the p spinors – for Hg the three p functions with the smallest exponents have the expansion coefficients 0.35, 0.74, and 0.19 the $p_{1/2}$ spinor, and 0.16, 0.76, and 0.30 for the $p_{3/2}$ spinor.

*Tl–Rn: (23, 21, 14:9, 9:10), Fr–Ra: (25, 21, 14:9, 9:10)*

Adding two more p functions is not enough to support a triple-zeta distribution and from Tl onwards a double-zeta p distribution is used. However, as the atomic number increases, the weight in this double-zeta distribution shifts more and more towards the largest exponent. Thus, for Tl the 6p expansion coefficients for the two most diffuse functions are 0.62 and 0.49 for $p_{1/2}$, and 0.48 and 0.65 for $p_{3/2}$, whereas the corresponding coefficients for Ra area 0.82, 0.31 and 0.70, 0.51. Throughout the series the outer p exponents show approximate even-tempered behavior.

*Ac: (25, 21, 16:9, 9:10), Th–Lr: (25, 21, 16:9, 12:10)*

All the actinides were optimized for the $s^2d^1f^n$ configuration. The addition of two d functions yields a distribution somewhere between double and triple zeta. For Ac the d function number 14 (i.e. the third most diffuse appears with expansion coefficient 0.16 in $5d_{3/2}$ and 0.09 in $6d_{3/2}$, and with 0.18 in $5d_{5/2}$ and 0.06 in $6d_{5/2}$. For Lr the corresponding coefficients are 0.07 in $5d_{3/2}$ and 0.20 in $6d_{3/2}$, 0.10 in $5d_{5/2}$ and 0.16 in $6d_{5/2}$. A similar effect is seen for the f functions which start out as a quadruple-zeta distribution for Th and end as a quintuple-distribution for Lr, although with small contributions from the most diffuse function. Again the increasing difference between finite basis and numerical calculations throughout the series is noteworthy. Reducing the number of f functions by 1 i.e. going to an 11:10 set, results in a further energy loss of 10–16 m$E_H$.

*Rf–112: (25, 21, 17:8, 12:10)*

For the fourth row of transition metals the electronic configuration $s^2d^n$ was used throughout. One more tight d function was added to accommodate the increasing number of electrons in the 6d shell, giving a triple-zeta distribution throughout. For the transition metals the f distribution starts out as quintuple zeta, but by the time we get to Uub (element. 112) function number 8 (the 5th most diffuse) is shared more or less equally between the 4f and 5f spinors.

*113–118: (25, 23, 17:8, 12:10)*

When the 7p spinors start filling up, the f distribution goes to quadruple zeta with the most diffuse f function assuming more and more a spectator role. For Uuo (118) the double-zeta s distribution shows a shift towards the tighter functions. The further addition of one more s function (to a total of 26) is found to lower the energy by approximately 10 m$E_H$. The spin-orbit splitting of the 7p spinors shows clearly in the expansion coefficients for the two most diffuse functions of the double-zeta representation: these are 0.88 and 0.21 for the $7p_{1/2}$ and 0.46 and 0.75 for the $7p_{3/2}$.

## 4 Discussion

As remarked previously, any basis set represents a compromise between accuracy (in some sense) and cost. The consequences of the choices made in arriving at this compromise are not always clear. For large basis sets, such as those considered here, the exponents can be optimized for the separate symmetries independently. There is only an insignificant gain in optimizing s and p exponents simultaneously, as compared to optimizing each set separately. On the other hand, the family feature which couples s and d exponents as well as p and f exponents tends to obscure the effects of changes made to the basis. Thus, the increase in the difference between analytical and numerical energy values as we traverse the lanthanide and actinide series may be due to insufficient description of the f spinors, but it could also at least partially be due to the fact that the increased number of f electrons changes the p exponents through the family coupling during the optimization process and that some of the energy loss comes from this.

For relativistic basis sets, there is an added complication relating to the quality criterion used. On the basis of the work of Talman [13], the Dirac–Hatree–Fock energy is considered to represent a minimum in the space of variational parameters for the positive energy states, but a maximum in the variational space for the negative energy states. As pointed out previously [9], the coupling of the exponents for the large and small components through the kinetic balance condition provides an implicit projection onto the positive energy states. However, in a truncated basis set this projection will only approximate the real energy surface spanned by the orbital rotations, and, therefore the minimum found in the exponent optimization may correspond to a point below the value obtained in fully numerical Dirac–Hartree–Fock calculations. Indeed, it may be shown that it is possible to force the total energy obtained from energy-minimized basis sets below that obtained in the numerical Dirac–Hartree–Fock calculations. Thus, a $\kappa$-based (25, 25, 23, 16, 16, 11, 11) set for element 118 yields an energy 22.5 $\mathrm{mE_H}$ below the numerical value. This is not a collapse of the variational process in the traditional sense (i.e. such as that observed when kinetic balance is not obeyed or if important parts of the electron repulsion are neglected), rather it represents the incompleteness of the basis set, and one might use the term prolapse to describe the phenomenon. For the use of an actual basis set, the possibility of a prolapse due to the minimization process certainly represents no greater problems than the energy deviation of any finite basis. Unfortunately, the use of total energy as a quality criterion to guide the optimization of the basis set is no longer unambiguous.

The danger of a prolapse is one reason for being somewhat restrictive with the size of the s and p sets. Experience has shown that it is, in particular, for these functions that a prolapse may be incurred. This increases the danger that attempts at improving the valence space through additional functions in the minimization process may lead to an unrealistic saturation of the inner function space. One way to avoid this is to freeze the inner functions when those core orbitals are sufficiently well described. This has not been done here, rather the optimization has been carried out without constraints, but with limited basis sets for these symmetries. These limitations on the s and p sets may lead to skewing of the function distribution, as indicated in some of the sets described earlier. A strategy for improving the valence descriptions of these sets is by adding functions to the valence space in the actual molecular calculations to ensure that the results are stable. Thus, it has been found that a (23, 21, 16:8, 10:10) basis should be supplemented with diffuse s and p functions as well as given an extended d range in order to produce stable bond lengths for TlAt.

Energy-minimized basis sets may also suffer from deficiencies in the region close to the nucleus. For the case of TlF this has been discussed by Quiney et al. [5]. A series expansion of the spinors in powers or $r$ close to the nucleus reveals that the ratio of the zeroth order term for the large and small component is not properly reproduced by a (25, 24, 16:8, 10:10) basis set for Tl. This will normally not affect calculations of chemical properties, but in calculations where the property expressions are sensitive to the quality of the small component, this behavior may be crucial. This was the case in the work of Quiney et al. [5], which dealt with processes of odd symmetry with respect to space and time inversion (PT-odd). For that particular application, a large even-tempered (34, 34, 16, 9) basis was preferred.

In this light, it is interesting to compare the energy-minimized sets with even-tempered sets where the exponents are chosen to form a geometric series. No such comparison can be totally unambiguous because the criteria chosen in developing the sets may differ. One approach is to regard the lowest possible total atomic energy as our criterion of quality and to investigate how the energy from the minimized set can be reproduced using an even-tempered set. This has been done for Kr and Rn by fixing the range of the exponents of the even-tempered sets to that of the minimized set (i.e. the largest and smallest exponents are the same for the two sets) and then investigating how many functions an even-tempered series must contain to produce the same energy. The fact that the symmetries are independent to a good approximation has been exploited by replacing the minimized set by even-tempered functions for one symmetry at a time. Thus, the exponents for p, d, and f functions are kept at their minimized (family basis) values, while the range of the s exponents are being spanned by an even-tempered set. The number of functions in the even-tempered set is then varied systematically until the energy is close to or lower than that of the minimized basis. The same procedure is repeated for the other symmetries. The results of this investigation are presented in Table 2, where the differences between the family basis set energy and the partial even-tempered basis value are listed.

Table 2 shows that the largest differences occur for the s and p orbitals; d and f sets are easily matched by even-tempered distributions. The slow convergence in the s basis for Rn has no practical significance, considering that the family value is 18.5 $\mathrm{mE_H}$ above the value from numerical calculations (see Table A3). With this

**Table 2.** Total atomic energies obtained by symmetrywise replacement of basis functions by even-tempered sets. Orb. – number and type of orbitals in even-tempered set, $\Delta E$ – energy difference in m$E_\mathrm{H}$ of relative minimized set

| Orb. | $\Delta E$ | Orb. | $\Delta E$ | Orb. | $\Delta E$ |
|---|---|---|---|---|---|
| Kr. Reference family set (19, 16, 11:8) | | | | | |
| 19*s* | 47.1 | 16*p* | 25.2 | 11*d* | 0.4 |
| 20*s* | 18.7 | 17*p* | 9.1 | | |
| 21*s* | 9.3 | 18*p* | 2.7 | | |
| 22*s* | 3.4 | 19*p* | 0.7 | | |
| 23*s* | 0.7 | 20*p* | 0.1 | | |
| 24*s* | −0.2 | | | | |
| Rn. Reference family set (23, 21, 14:9, 9:10) | | | | | |
| 23*s* | 106.8 | 21*p* | 870.7 | 14*d* | 12.9 |
| 24*s* | 55.8 | 22*p* | 378.1 | 15*d* | 2.1 |
| 25*s* | 21.4 | 23*p* | 152.8 | 16*d* | −0.4 |
| 26*s* | 9.7 | 24*p* | 75.0 | | |
| 27*s* | 5.9 | 25*p* | 27.8 | 9*f* | 0.9 |
| 28*s* | 2.9 | 26*p* | 6.7 | 10*f* | 0.3 |
| 29*s* | 1.5 | 27*p* | 0.7 | | |
| 30*s* | 1.1 | 28*p* | −0.3 | | |
| 31*s* | 0.8 | | | | |
| 32*s* | 0.4 | | | | |
| 33*s* | 0.2 | | | | |
| 34*s* | 0.1 | | | | |
| 35*s* | 0.0 | | | | |
| 36*s* | −0.3 | | | | |

level of accuracy energy differences of 1.5 $\mathrm{mE_H}$ are acceptable. Thus, for Kr, where the family value is 3.0 $\mathrm{mE_H}$ above the numerical value, it appears from Table 2 that an even-tempered set requires four more s functions and three more p functions than the family set, while for Rn one would require at least five more s functions, five p functions, and one d function; however, these estimates do not take the family property into account. If one wants to retain this (over the same exponent span), the requirements on the even-tempered sets increase somewhat. Further calculations show that we need a (24, 19, 11:13) even-tempered basis to match the energy of the minimized (19, 16, 11:8) family set. Similarly for Rn we need a (30, 27, 16, 15, 9, 15) even-tempered set to match the family (23, 21, 14:9, 9:10). Comparisons such as this should be regarded with some caution. First of all, one may have different goals in developing even-tempered basis sets than for energy-optimized sets, as was the case in Ref. [5]. Secondly, the possibility of a prolapse in energies may influence the comparisons; this is likely to work in favor of the energy-minimized basis, although even-tempered basis sets are not immune to this problem either. The strong points of the two types of basis sets are different and thus a comparison can never be completely fair.

Despite the possible shortcomings, the present series of basis sets should provide increased opportunities for researchers in need of doing four component relativistic calculations. The basis sets have also proven to be useful for generating basis sets to be used with various scalar approximations to relativistic calculations. Ultimately the true merits of any basis set will only emerge through extensive applications. These basis sets are currently being tried in a number of calculations and from the experiences gained it will hopefully be possible to gain further insight into the requirements for good basis sets to be used in four-component calculations. This, together with improved algorithms for exponent optimization, should eventually provide selections of basis sets which place relativistic calculations on an equal footing with non-relativistic work in this respect.

The present basis sets are available as supplementary electronic material in the form of downloadable ASCII files.

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## Appendix

The total energies obtained with the present series of basis sets are listed here for the separate elements. The

**Table A1.** Total energies in $E_\mathrm{H}$ for K–Kr. $\Delta E$ is the deviation from the numerical value in $\mathrm{m}E_\mathrm{H}$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| K | 39.000 | $-6.015256451360 \times 10^{2}$ | 0.3 |
| Ca | 40.000 | $-6.797098655636 \times 10^{2}$ | 0.3 |
| Sc | 45.000 | $-7.633778818069 \times 10^{2}$ | 0.9 |
| Ti | 48.000 | $-8.528188190043 \times 10^{2}$ | 1.0 |
| V | 51.000 | $-9.481874939726 \times 10^{2}$ | 1.2 |
| Cr | 52.000 | $-1.049594306272 \times 10^{3}$ | 1.7 |
| Mn | 55.000 | $-1.157320376215 \times 10^{3}$ | 1.5 |
| Fe | 56.000 | $-1.271390219774 \times 10^{3}$ | 1.8 |
| Co | 59.000 | $-1.391999818166 \times 10^{3}$ | 2.0 |
| Ni | 58.000 | $-1.519293511020 \times 10^{3}$ | 2.9 |
| Cu | 63.000 | $-1.653451847858 \times 10^{3}$ | 3.2 |
| Zn | 64.000 | $-1.794610054588 \times 10^{3}$ | 3.0 |
| Ga | 69.000 | $-1.942560919754 \times 10^{3}$ | 2.8 |
| Ge | 74.000 | $-2.097467572390 \times 10^{3}$ | 2.8 |
| As | 75.000 | $-2.259439110959 \times 10^{3}$ | 2.8 |
| Se | 80.000 | $-2.428585445554 \times 10^{3}$ | 2.8 |
| Br | 79.000 | $-2.605020578042 \times 10^{3}$ | 2.9 |
| Kr | 84.000 | $-2.788857635865 \times 10^{3}$ | 3.0 |

**Table A2.** Total energies in $E_\mathrm{H}$ for Rb–Xe. $\Delta E$ is the deviation from the numerical value in $\mathrm{m}E_\mathrm{H}$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| Rb | 85.000 | $-2.979801174098 \times 10^{3}$ | 3.8 |
| Sr | 88.000 | $-3.178076282939 \times 10^{3}$ | 3.7 |
| Y | 89.000 | $-3.383756531085 \times 10^{3}$ | 5.3 |
| Zr | 90.000 | $-3.597077640522 \times 10^{3}$ | 5.7 |
| Nb | 93.000 | $-3.818162171798 \times 10^{3}$ | 6.1 |
| Mo | 98.000 | $-4.047134230960 \times 10^{3}$ | 7.4 |
| Tc | 98.000 | $-4.284106409565 \times 10^{3}$ | 7.0 |
| Ru | 102.000 | $-4.529206421196 \times 10^{3}$ | 7.5 |
| Rh | 103.000 | $-4.782554881469 \times 10^{3}$ | 8.0 |
| Pd | 106.000 | $-5.044383626721 \times 10^{3}$ | 9.1 |
| Ag | 107.000 | $-5.314624678347 \times 10^{3}$ | 9.6 |
| Cd | 114.000 | $-5.593309230366 \times 10^{3}$ | 9.7 |
| In | 115.000 | $-5.880422174718 \times 10^{3}$ | 9.5 |
| Sn | 120.000 | $-6.176118521785 \times 10^{3}$ | 9.6 |
| Sb | 121.000 | $-6.480508904932 \times 10^{3}$ | 9.8 |
| Te | 130.000 | $-6.793689198032 \times 10^{3}$ | 9.9 |
| I | 127.000 | $-7.115784224790 \times 10^{3}$ | 10.0 |
| Xe | 132.000 | $-7.446885328181 \times 10^{3}$ | 10.2 |

**Table A3.** Total energies in $E_\mathrm{H}$ for Cs, Ba, and Hf–Rn. $\Delta E$ is the deviation from the numerical value in $\mathrm{m}E_\mathrm{H}$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| Cs | 133.000 | $-7.786767388085 \times 10^{3}$ | 4.3 |
| Ba | 138.000 | $-8.135640837571 \times 10^{3}$ | 4.2 |
| Hf | 180.000 | $-1.508876937130 \times 10^{4}$ | 17.3 |
| Ta | 181.000 | $-1.561661388950 \times 10^{4}$ | 16.9 |
| W | 184.000 | $-1.615611955901 \times 10^{4}$ | 18.3 |
| Re | 187.000 | $-1.670760327942 \times 10^{4}$ | 16.8 |
| Os | 192.000 | $-1.727106541071 \times 10^{4}$ | 17.0 |
| Ir | 193.000 | $-1.784677137067 \times 10^{4}$ | 17.4 |
| Pt | 195.000 | $-1.843489825444 \times 10^{4}$ | 18.9 |
| Au | 197.000 | $-1.903552398733 \times 10^{4}$ | 19.4 |
| Hg | 202.000 | $-1.964887737403 \times 10^{4}$ | 18.8 |
| Tl | 205.000 | $-2.027483307036 \times 10^{4}$ | 17.6 |
| Pb | 208.000 | $-2.091369690473 \times 10^{4}$ | 17.4 |
| Bi | 209.000 | $-2.156568855177 \times 10^{4}$ | 17.5 |
| Po | 209.000 | $-2.223099537520 \times 10^{4}$ | 17.8 |
| At | 205.000 | $-2.290978942652 \times 10^{4}$ | 18.2 |
| Rn | 222.000 | $-2.360208573761 \times 10^{4}$ | 18.5 |

**Table A4.** Total energies in $E_H$ for La–Lu. $\Delta E$ is the deviation from the numerical value in m$E_H$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| La | 139.000 | $-8.493640636347 \times 10^3$ | 5.1 |
| Ce | 140.000 | $-8.861065360862 \times 10^3$ | 6.1 |
| Pr | 141.000 | $-9.238192797527 \times 10^3$ | 6.8 |
| Nd | 144.000 | $-9.625156943946 \times 10^3$ | 7.5 |
| Pm | 145.000 | $-1.002210456018 \times 10^4$ | 7.1 |
| Sm | 152.000 | $-1.042915926376 \times 10^4$ | 8.8 |
| Eu | 162.000 | $-1.084649308114 \times 10^4$ | 9.6 |
| Gd | 158.000 | $-1.127421980907 \times 10^4$ | 10.4 |
| Dy | 159.000 | $-1.171251562136 \times 10^4$ | 11.2 |
| Tb | 162.000 | $-1.216151122796 \times 10^4$ | 12.2 |
| Ho | 162.000 | $-1.262137551311 \times 10^4$ | 13.2 |
| Er | 168.000 | $-1.309223099952 \times 10^4$ | 14.2 |
| Tm | 168.934 | $-1.357427746806 \times 10^4$ | 15.4 |
| Yb | 173.040 | $-1.406764292033 \times 10^4$ | 16.6 |
| Lu | 175.000 | $-1.457251561522 \times 10^4$ | 17.9 |

**Table A5.** Total energies in $E_H$ for Fr, Ra, and Rf–118. $\Delta E$ is the deviation from the numerical value in rm$E_H$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| Fr | 223.000 | $-2.430817590650 \times 10^4$ | 17.4 |
| Ra | 226.000 | $-2.502817080236 \times 10^4$ | 17.0 |
| Rf | 261.000 | $-3.869392618306 \times 10^4$ | 29.1 |
| Db | 262.000 | $-3.969951118221 \times 10^4$ | 29.3 |
| Sg | 263.000 | $-4.072525040477 \times 10^4$ | 29.5 |
| Bh | 262.000 | $-4.177189876379 \times 10^4$ | 29.9 |
| Hs | 265.000 | $-4.283923463686 \times 10^4$ | 30.0 |
| Mt | 266.000 | $-4.392857149454 \times 10^4$ | 30.3 |
| 110 | 281.160 | $-4.503792564225 \times 10^4$ | 29.6 |
| 111 | 283.716 | $-4.617206066629 \times 10^4$ | 29.6 |
| 112 | 286.272 | $-4.732974568929 \times 10^4$ | 29.5 |
| 113 | 288.828 | $-4.851140295249 \times 10^4$ | 20.6 |
| 114 | 291.384 | $-4.971786061746 \times 10^4$ | 19.4 |
| 115 | 293.940 | $-5.094989582797 \times 10^4$ | 18.7 |
| 116 | 296.496 | $-5.220832498275 \times 10^4$ | 18.0 |
| 117 | 299.052 | $-5.349401472542 \times 10^4$ | 17.2 |
| 118 | 301.608 | $-5.480788640140 \times 10^4$ | 16.3 |

**Table A6.** Total energies in $E_H$ for Ac–Lr. $\Delta E$ is the deviation from the numerical value in m$E_H$

| Atom | Atomic mass no. | Energy | $\Delta E$ |
|---|---|---|---|
| Ac | 227.000 | $-2.576234953450 \times 10^4$ | 17.8 |
| Th | 232.000 | $-2.651082745494 \times 10^4$ | 19.8 |
| Pa | 231.000 | $-2.727435803651 \times 10^4$ | 20.8 |
| U | 238.000 | $-2.805281824909 \times 10^4$ | 21.7 |
| Np | 237.000 | $-2.884698306169 \times 10^4$ | 23.0 |
| Pu | 244.000 | $-2.965661040768 \times 10^4$ | 24.4 |
| Am | 243.000 | $-3.048258758961 \times 10^4$ | 26.3 |
| Cm | 247.000 | $-3.132472750354 \times 10^4$ | 28.3 |
| Bk | 247.000 | $-3.218374964495 \times 10^4$ | 25.2 |
| Cf | 251.000 | $-3.305960561870 \times 10^4$ | 27.3 |
| Es | 252.000 | $-3.395301230378 \times 10^4$ | 28.7 |
| Fm | 257.000 | $-3.486393233886 \times 10^4$ | 30.1 |
| Md | 258.000 | $-3.579325007989 \times 10^4$ | 31.6 |
| No | 259.000 | $-3.674113437439 \times 10^4$ | 33.2 |
| Lr | 260.000 | $-3.770801055971 \times 10^4$ | 34.9 |

elements are grouped according to the rows of the periodic system, with lanthanides and actinides as separate groups. The values listed here are those calculated as weighted average energies from the GRASP program. As explained previously a Gaussian charge distribution is chosen for the finite nucleus. In our approach the exponent of this distribution is determined from the atomic mass number and as the total energy depends on the mass numbers used, they are included in tables A1, A2, A3, A4, A5, and A6.

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