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REGULAR ARTICLE

Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the actinides Ac–Lr

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Abstract Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized for the actinide elements Ac–Lr. The basis sets include SCF exponents for the occupied spinors and for the 7p shell, exponents of correlating functions for the valence shells (5f, 6d and 7s) and the outer core shells (5d, 6s and 6p), and diffuse functions including functions for dipole polarization of the 5f shell. A finite nuclear size was used in all optimizations. Prescriptions are given for constructing contracted basis sets. The basis sets are available as an internet archive and from the Dirac program web site, http://dirac.chem.sdu.dk.

Keywords Gaussian basis sets · Relativistic basis sets · Actinide elements · Double zeta · Triple zeta · Quadruple zeta · Correlating functions

1 Introduction

The growing use of all-electron relativistic methods for heavy-element chemistry has stimulated work on basis sets that include relativistic effects [1–21]. Many of these all-electron basis sets only include basis functions that describe the SCF occupied orbitals, and do not include correlating functions. This paper is one of a series of papers [14–18] presenting relativistic basis sets that include diffuse functions and valence and outer core correlating functions in addition to the SCF sets. One of the goals of the present series is to provide basis sets in the style of the correlation-consistent sets [22–25] that give fairly uniform quality across a range of elements, and preferably across the whole periodic table. The focus of this paper is basis sets for the actinide elements, Ac–Lr.

The actinides present somewhat of a challenge in this respect, because the series starts out as a d block and ends up as an f block, and the 6d orbital is occupied for several members of the series (Ac, Th, Pa, U, Np, Cm, and Lr). For the rest of the series, the 6d orbital is relatively low-lying and must be treated with the rest of the orbitals in the basis set optimization. For this reason, the 6d shell must be counted in the occupied set for the whole series, and correlating functions must be optimized for the 6d as well as for the 5f shell. Likewise, the 7p shell must be included at least for polarization of the 7s and 6d – and for Lr, the ground state has the $7p_{1/2}$ occupied, not the $6d_{3/2}$, although the latter is low-lying [26]. Correlation of the 6s and 6p shells is critical, too, because these shells are in the valence region of the ions and are involved in the bonding in species like UO_2^{2+}. In addition, the 5f shell goes from an empty shell at the beginning of the series to a valence shell in the early part, to an outer core shell at the end. This change affects the design of the basis set in the choice of functions for polarization and correlation. Finally, for outer core correlation, the 5d shell must be considered.

2 Methods

The methods used have been described previously [14–16,27,28]. The basis sets were optimized in Dirac–Hartree–Fock calculations using the Dirac–Coulomb Hamiltonian with the standard Gaussian nuclear charge distribution [29]. As for the previous basis sets, ℓ-optimization was employed. In the SCF optimizations,

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the exponents are varied only within a given angular space, i.e., for a given ℓ value, with all other exponents fixed. The exponents in each angular space are to a large degree independent of the other angular spaces. The angular spaces are cycled through the optimization process until there is no significant change in the total energy and the gradient with respect to the logarithms of the exponents.

The size of the basis sets was determined by a series of optimizations on the uranium atom and on the lawrencium atom. The series was determined by first fully optimizing a reference basis set, then performing optimizations within each angular space for different numbers of exponents with the exponents in the other angular spaces fixed. The balance between the energy gain in each angular space for the addition of the next function, the representation of the outermost maximum of the valence and outer core shells, and the match with the already published basis sets for the 6p main group elements were used to decide on the optimum basis set.

The variable occupancy of the 5f and the 6d presents some challenges in the SCF basis set optimization. For Ac and Th, the ground state $6d^n$ $7s^2$ configuration was used to optimize the s, p, and d exponent sets. Ac was treated as a d transition metal for the purposes of optimization. The 5f shell was entirely omitted and the f exponent set was also optimized on the ground state occupation. The size of the f set for Ac was the same as for Rn in the 6p sets [14–17]. The 5f in Th is close to being occupied, so the 5f was retained in the optimizations, and the f exponent set was optimized on the $5f^1$ $6d^1$ $7s^2$ configuration.

For the remaining elements, from Pa to Lr, the s, p, and f sets were optimized on the ground configuration, which is $5f^{n-1}$ $6d^1$ $7s^2$ for Pa, U, Np, Cm, and Lr, and $5f^n$ $7s^2$ for the rest. The d set was optimized on the $5f^{n-1}$ $6d^1$ $7s^2$ configuration for all elements from Pa to Lr, in order to obtain a representation of the 6d orbital, which is critical in the bonding of the actinyls.

After optimizing the SCF sets, functions were added to describe the 7p shell, which is generally added for polarization of the 7s orbital, and is actually occupied in Lr, due to the relativistic contraction. These functions were optimized by replacing the two 7s electrons with two 7p electrons. Two functions were added to the double-zeta basis sets, three to the triple-zeta, and four to the quadruple-zeta. These functions were optimized along with the functions for the outermost maximum of the 6p shell for the double-zeta and triple-zeta basis sets, and with the functions for all the maxima except the 2p shell for the quadruple-zeta basis sets. The reason for this last choice is that the exponents are closer in the quadruple-zeta basis sets, and the changes in the exponents are more strongly coupled. The reason for re-optimizing more than just the added functions is that the spacing of the exponents for the 6p orbital is larger than for the inner orbitals because the outermost exponents must approximate the exponential tail of the orbital as well as the maximum. With the addition of functions that are more diffuse, the exponents for the 6p no longer need to describe the tail, and can be re-optimized.

As for the p and d blocks, the number of exponents that describes the outermost maximum of the s and p shells determines the basis set designation. This number is usually also the number of exponents in the next outermost maximum of the s and p shells. The general principle for maintaining a reasonable balance is that the second shell for a given ℓ has one more function than the basis set designation, and the d and f shells have an extra function. For example, the 2s shell usually has one more function for its outermost maximum than higher s shells. Thus, the 5d and 6d orbitals have three, four, and five exponents for the outermost maximum for the double-zeta, triple-zeta, and quadruple-zeta basis sets, and the 5f orbitals have four, five, and six exponents for the outermost f maximum for the double-zeta, triple-zeta, and quadruple-zeta basis sets.

Correlating functions for the 5d, 5f, 6s, 6p, 6d, and 7s shells were optimized in MR-SDCI calculations, using the RAMCI program [28] modified for basis set optimization. The procedure for the various shells is described below.

For the 5f shell the functions were optimized on the ground f^ns^2 or $f^{n-1}d^1s^2$ configuration. Only configuration state functions (CSF) coupling to the ground state *J* value were included in the optimization, mainly due to the large number of such CSF. The correlating sets were 1g for the double-zeta basis sets, 2g1h for triple-zeta, and 3g2h1i for quadruple-zeta. For the quadruple-zeta basis sets it was necessary to split the correlating set into a 3g set and a 2h1i set for elements in the middle of the block due to the number of configurations. Since the angular spaces are fairly well decoupled, this is not a serious approximation.

For the 6d and 7s shells, correlating functions were optimized on the $f^{n-1}d^1s^2$ configuration, except for Th and Ac, for which the d^ns^2 configuration was used. The correlating sets were 1f for the double-zeta basis sets, 2f1g for triple-zeta, and 3f2g1h for quadruple-zeta. For the quadruple-zeta basis sets, the 5f shell was coupled to the highest possible angular momentum to reduce the number of configurations to a minimum. Since the f shell is only providing a static potential, this approximation has little impact on the results.

Correlating functions for the 6s and 6p shells were optimized in MR-SDCI calculations on the ground $f^n s^2$ or $f^{n-1}d^1s^2$ configuration, for the state with the maximum J value. Single and double excitations out of the 6s and 6p shells were coupled to $J = 0$, to ensure that only configurations representing 6s and 6p correlation were included. The correlating sets were 1d for the double-zeta basis sets, 2d1f for triple-zeta, and 3d2f1g for quadruple-zeta.

Correlating functions for the 5d shell were optimized on the same configurations, with single and double excitations out of the 5d shell coupled to $J = 0$. The correlating sets were 1f for the double-zeta basis sets, 2f1g for triple-zeta, and 3f2g1h for quadruple-zeta.

Functions for dipole polarization of the 6d and the 5f shells were determined as follows. For the double-zeta basis sets, a single f function was determined for the 6d dipole polarization and a single g function was determined for the 5f dipole polarization by maximizing the polarizability calculated by second-order perturbation theory. The basis states for the perturbation theory consisted of the eigenfunctions of the Dirac Hamiltonian for the configurations generated by a single d → f excitation from the $f^{n-1}d^1s^2$ configuration for the 6d dipole polarization, and by a single f → g excitation from the $f^n s^2$ configuration for the 5f dipole polarization. The latter is not the ground state for a number of the atoms, but the gradient of the polarizability with the exponent is small, so the change in configuration does not have a large effect on the polarizability. For the triple-zeta and quadruple-zeta basis sets, the exponents of the dipole polarization functions were determined by applying the ratio of the exponents of the dipole polarizing function to the correlating function for the double-zeta basis set to the outermost correlating function in each angular momentum. In this way, 1f1g and 1f1g1h sets for 6d dipole polarization and 1g1h and 1g1h1i sets for 5f dipole polarization were generated for the triple-zeta and quadruple-zeta basis sets. These functions are referred to below as “dipole polarization functions”, to distinguish this term from the commonly used but less specific term “polarization functions”, which generally refers to functions of higher angular momentum than the valence orbitals without much regard to radial extent or purpose.

Contraction coefficients for the occupied spinors, including the 6d and 7p, were taken from SCF calculations on a weighted average of the valence configurations, as follows:

- For Ac, Pa, U, Np, Cm, and Lr, where the 6d is occupied in the ground state, the $5f^{n-1}$ $6d^1$ $7s^2$ and $5f^{n-1}$ $7p^1$ $7s^2$ configurations were used with a 100:6 weight ratio. Note that for Ac the 5f is empty: this element is treated as a transition metal.
- For Th, the $6d^2$ $7s^2$, $5f^1$ $6d^1$ $7s^2$ and $6d^1$ $7s^2$ $7p^1$ configurations were used, with a weight ratio of 100:10:6.
- For the rest (Pu, Am, Cf–No), the $5f^n$ $7s^2$, $5f^{n-1}$ $6d^1$ $7s^2$, and $5f^{n-1}$ $7p^1$ $7s^2$ configurations were used with a weight ratio of 100:10:6.

To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed on several of the elements across the row, in which different primitive functions were included in the correlating space. For each basis set size, the appropriate number of primitive functions was used in the MRCI calculations. For example, for 6s6p correlation in the triple-zeta basis sets, the correlating set was 2s2p2d1f. Excitations into the 5f shell were not considered in these calculations. The large and small component coefficients of these correlating functions were determined by diagonalizing the Fock matrix in the space of the DHF occupied functions plus the primitive functions, and orthogonalizing the resultant extra functions to the DHF occupied functions.

3 Primitive basis sets

The SCF basis set sizes including the p functions for the 7p orbital are 26s23p17d10f for the dz set, 33s29p21d12f for the tz set, and 37s34p24d14f for the qz set, for all except Ac, where the basis set sizes are 26s23p17d8f, 33s29p21d10f, and 37s34p24d12f.

Configuration average total energies for the ground configuration from calculations using these basis sets, uncontracted, are compared with the numerical values in Table 1. The energies for some elements in the qz sets go below the numerical limit, because the kinetic balance condition imposed on the exponents only ensures that the energy is in error by no more than the order of c^{-4}. The energy optimization is in fact bounded from below, and cannot collapse, but it does not converge to the numerical Dirac–Fock energy. This phenomenon is known as “prolapse” [12], and only matters for properties that are sensitive to the details of the wave function near the nucleus [30]. For these properties, it is preferable to replace the core part of the basis set with an even-tempered sequence of exponents.

The correlating and dipole polarizing exponents for the double zeta basis sets are presented in Table 2. The only point to note is that the dipole polarizing f function for the 6d of Th is somewhat larger because the d is doubly occupied and is less diffuse than for the other actinides.

Table 1 Configuration average total SCF energies in E_h for uncontracted basis set and numerical calculations on the ground configuration

Element	Double-zeta	Triple-zeta	Quadruple-zeta	Numerical
Ac	−25762.358998	−25762.368882	−25762.369223	−25762.368035
Th	−26510.896910	−26510.908510	−26510.908703	−26510.907412
Pa	−27274.364635	−27274.379259	−27274.380212	−27274.378808
U	−28052.824733	−28052.840474	−28052.841554	−28052.641562
Np	−28846.989887	−28847.006808	−28847.007886	−28847.006095
Pu	−29656.597488	−29656.617971	−29656.619493	−29656.617513
Am	−30482.603352	−30482.624862	−30482.626384	−30482.624157
Cm	−31324.735654	−31324.757175	−31324.758424	−31324.755852
Bk	−32183.817012	−32183.840661	−32183.842286	−32183.839453
Cf	−33059.698984	−33059.723737	−33059.725484	−33059.722284
Es	−33953.131070	−33953.157160	−33953.158912	−33953.155319
Fm	−34864.075869	−34864.103278	−34864.105101	−34864.101042
Md	−35793.417695	−35793.446548	−35793.448451	−35793.443897
No	−36741.325462	−36741.355793	−36741.357837	−36741.352732
Lr[a]	−37707.849193	−37707.878132	−37707.879999	−37707.874213

[a] 6d^1 configuration

Table 2 Exponents of correlating and dipole polarizing functions for the double-zeta basis sets

Element	5f corr g	5f pol g	6d/7s corr f	6d pol f	5d corr f
Ac			8.92398E−02	6.24908E−02	2.37018E+00
Th	1.00610E+00	1.95597E−01	2.58207E−01	8.67664E−02	2.52820E+00
Pa	1.35525E+00	2.28360E−01	9.81988E−02	6.59017E−02	3.17744E+00
U	1.52001E+00	2.61889E−01	1.02979E−01	6.56835E−02	3.37830E+00
Np	1.65956E+00	2.93353E−01	1.05801E−01	6.95427E−02	3.57611E+00
Pu	1.74363E+00	2.87696E−01	1.08916E−01	7.13232E−02	3.69382E+00
Am	1.88203E+00	3.22853E−01	1.11778E−01	7.10962E−02	3.89204E+00
Cm	2.06887E+00	3.51390E−01	1.15930E−01	6.78858E−02	4.16448E+00
Bk	2.20863E+00	3.80329E−01	1.21013E−01	6.74231E−02	4.28534E+00
Cf	2.36324E+00	4.09423E−01	1.24964E−01	6.56869E−02	4.48373E+00
Es	2.51442E+00	4.37041E−01	1.29420E−01	6.42382E−02	4.68370E+00
Fm	2.66593E+00	4.63965E−01	1.34128E−01	6.40869E−02	4.88526E+00
Md	2.81827E+00	4.92220E−01	1.40087E−01	6.25639E−02	5.08863E+00
No	2.97334E+00	5.21963E−01	1.45588E−01	6.04917E−02	5.29400E+00
Lr	3.20999E+00	7.16871E−01	1.52542E−01	5.66240E−02	5.58124E+00

The exponents of the 5f correlating 2g1h functions for the triple-zeta basis sets are given in Table 3. Two minima were found for the triple-zeta 6d correlating 2f1g functions for elements in the middle of the block: one in which the two f functions were tighter and one in which the two f functions were more diffuse. The energies of these minima are given in Table 4. The difference between the minima is only a few tens of microhartrees. For the early actinides, only the tighter minimum could be found, and for Md and No, only the more diffuse minimum could be found. This means that there was no single consistent set across the row. However, the tighter correlating f exponents are represented reasonably well in the SCF set, and with an even-tempered extension of one function, the correlating space for the 6d is well covered. The g exponent is very similar for the two minima. Where there were two minima, the exponent from the tighter minimum was taken. The g exponents are given in Table 5 along with the dipole polarizing f and g exponents.

Table 3 Exponents of 5f correlating 2g1h functions for the triple-zeta basis sets

Element	g	g	h
Th	1.76856E+00	4.93675E−01	1.01944E+00
Pa	2.38481E+00	7.28704E−01	1.31754E+00
U	2.65106E+00	8.23542E−01	1.53702E+00
Np	2.86396E+00	9.02525E−01	1.77993E+00
Pu	2.97486E+00	9.22103E−01	1.95865E+00
Am	3.19431E+00	9.97569E−01	2.17376E+00
Cm	3.58892E+00	1.16469E+00	2.43969E+00
Bk	3.67841E+00	1.17584E+00	2.43881E+00
Cf	3.91274E+00	1.26000E+00	2.62621E+00
Es	4.13978E+00	1.34081E+00	2.79924E+00
Fm	4.36902E+00	1.42193E+00	2.96014E+00
Md	4.59942E+00	1.50322E+00	3.14533E+00
No	4.83593E+00	1.58608E+00	3.37224E+00
Lr	5.21759E+00	1.75444E+00	3.63693E+00

The dipole polarizing g exponent for the 6d was determined by even-tempered extension of the correlating set, as described in Sect. 2, and the dipole polarizing

Table 4 Total energies for the two minima found in the optimization of the 2f1g correlating functions for the 6d and 7s shells

Element	Higher f exponents	Lower f exponents
Ac	−25762.385620	No minimum
Th	−26510.941925	No minimum
Pa	−27274.486918	No minimum
U	−28053.016472	No minimum
Np	−28847.240841	−28847.240839
Pu	−29656.915961	−29656.915977
Am	−30482.945288	−30482.945297
Cm	−31325.169755	−31325.169771
Bk	−32184.125945	−32184.125980
Cf	−33059.942182	−33059.942210
Es	−33953.321058	−33953.321101
Fm	−34864.181743	−34864.181783
Md	No minimum	−35793.420135
No	No minimum	−36741.236582
Lr	−37707.894216	−37707.894270

Table 5 Exponents of 6d/7s correlating g function and 6d dipole polarizing 1f1g functions for the triple-zeta basis sets

Element	corr g	pol f	pol g
Ac	1.38719E−01	6.24908E−02	9.71390E−02
Th	2.10593E−01	8.67664E−02	7.07664E−02
Pa	1.88376E−01	6.59017E−02	1.26420E−01
U	1.74963E−01	6.56835E−02	1.11597E−01
Np	1.73523E−01	6.95427E−02	1.14056E−01
Pu	1.83887E−01	7.13232E−02	1.20418E−01
Am	1.77917E−01	7.10962E−02	1.13164E−01
Cm	1.80836E−01	6.78858E−02	1.05893E−01
Bk	1.95449E−01	6.74231E−02	1.08896E−01
Cf	1.94218E−01	6.56869E−02	1.02090E−01
Es	1.97873E−01	6.42382E−02	9.82152E−02
Fm	1.97915E−01	6.40869E−02	9.45648E−02
Md	2.04672E−01	6.25639E−02	9.14079E−02
No	2.09462E−01	6.04917E−02	8.70310E−02
Lr	1.98739E−01	5.66240E−02	7.37725E−02

f function was taken from the dz set. Functions for dipole polarization of the 5f are given in Table 6.

Functions for correlation of the 5d are given in Table 7. The g exponent is close to the larger of the g exponents for 5f correlation for most of the block, and therefore need not be included in the basis sets. Likewise, the f functions can be represented by uncontracting functions from the SCF f set.

No particular problems were encountered in the optimization of the quadruple-zeta correlating sets. However, the irregularity of the g set for 6d correlation is an indication of the flatness of the potential energy surface, and it is probably not a serious restriction to omit the larger exponent, since it is close to the smallest g exponent for 5f correlation for the first half of the block at least.

Table 6 Exponents of 5f dipole polarizing 1g1h functions for the triple-zeta basis sets

Element	g	h
Pa	1.22787E−01	2.22007E−01
U	1.41892E−01	2.64820E−01
Np	1.59535E−01	3.14630E−01
Pu	1.52145E−01	3.23173E−01
Am	1.71128E−01	3.72897E−01
Cm	1.97819E−01	4.14373E−01
Bk	2.02482E−01	4.19966E−01
Cf	2.18290E−01	4.54980E−01
Es	2.33053E−01	4.86548E−01
Fm	2.47466E−01	5.15169E−01
Md	2.62542E−01	5.49343E−01
No	2.78434E−01	5.91989E−01
Lr	3.91810E−01	8.12219E−01

Table 7 Exponents of 5d correlating 2f1g functions for the triple-zeta basis sets

Element	f	f	g
Ac	3.56354E+00	1.48979E+00	2.81301E+00
Th	3.77800E+00	1.59904E+00	2.98950E+00
Pa	4.26721E+00	2.02738E+00	3.09510E+00
U	4.49004E+00	2.16228E+00	3.25343E+00
Np	4.71095E+00	2.29465E+00	3.41250E+00
Pu	4.88082E+00	2.34551E+00	3.55786E+00
Am	5.10479E+00	2.47703E+00	3.71969E+00
Cm	5.37632E+00	2.68919E+00	3.89740E+00
Bk	5.55284E+00	2.73394E+00	4.04574E+00
Cf	5.77997E+00	2.86392E+00	4.21171E+00
Es	6.00950E+00	2.99518E+00	4.37977E+00
Fm	6.24148E+00	3.12745E+00	4.54983E+00
Md	6.47597E+00	3.26103E+00	4.72199E+00
No	6.71328E+00	3.39597E+00	4.89632E+00
Lr	6.99784E+00	3.63108E+00	5.08890E+00

The exponents of the quadruple-zeta correlating functions for the 5f are given in Table 8, for the 6d and 7s in Table 9, for the 6s and 6p in Table 10, and for the 5d in Table 11. Functions for correlation of the 6s and 6p were determined because this set includes a g function, and it was necessary to determine whether the g function was represented in the correlating set for the 5f or not. As is evident from the values presented below, the space covered by this exponent is indeed mapped by the correlating set for the 5f.

The quadruple-zeta dipole polarizing sets were determined as described in Sect. 2, and are given in Tables 12 and 13.

4 Contraction patterns

The MR-SDCI calculations that were performed to determine which functions to uncontract yielded the

Table 8 Exponents of 5f correlating 3g2h1i functions for the quadruple-zeta basis sets

Element	g	g	g	h	h	i
Th	2.62680E+00	8.96025E−01	2.85355E−01	1.71755E+00	5.09950E−01	1.35140E+00
Pa	3.55979E+00	1.30926E+00	4.64157E−01	2.20678E+00	7.05555E−01	1.80003E+00
U	3.92105E+00	1.46395E+00	5.26358E−01	2.52428E+00	8.33989E−01	1.99192E+00
Np	4.19146E+00	1.58845E+00	5.78202E−01	2.80839E+00	9.61275E−01	2.15840E+00
Pu	4.27827E+00	1.61160E+00	5.71929E−01	3.04161E+00	1.06117E+00	2.27550E+00
Am	4.55947E+00	1.72885E+00	6.18552E−01	3.28556E+00	1.17011E+00	2.54086E+00
Cm	5.03617E+00	1.98751E+00	7.48935E−01	3.45690E+00	1.22635E+00	2.85035E+00
Bk	5.08356E+00	1.98388E+00	7.26078E−01	3.61122E+00	1.27370E+00	2.94200E+00
Cf	5.51037E+00	2.20059E+00	8.30203E−01	3.98829E+00	1.45713E+00	3.24163E+00
Es	5.69080E+00	2.25399E+00	8.34148E−01	4.18267E+00	1.53709E+00	3.35035E+00
Fm	6.05429E+00	2.42114E+00	8.97991E−01	4.41786E+00	1.63458E+00	3.38371E+00
Md	6.34685E+00	2.55221E+00	9.49770E−01	4.65881E+00	1.73885E+00	3.56804E+00
No	6.65383E+00	2.68787E+00	1.00296E+00	4.92981E+00	1.87148E+00	3.75398E+00
Lr	7.20276E+00	2.97032E+00	1.14529E+00	5.29377E+00	2.06510E+00	4.05563E+00

Table 9 Exponents of 6d/7s correlating 3f2g1h functions for the quadruple-zeta basis sets

Element	f	f	f	g	g	h
Ac	4.73082E−01	1.50442E−01	7.97408E−02	3.30653E−01	1.11090E−01	1.66219E−01
Th	2.28737E+00	5.32527E−01	1.49999E−01	3.62201E−01	1.25406E−01	2.77581E−01
Pa	4.51104E−01	1.57685E−01	8.33208E−02	5.75250E−01	1.48428E−01	1.82852E−01
U	4.64869E−01	1.66329E−01	8.55602E−02	3.99589E−01	1.31195E−01	1.93250E−01
Np	4.90600E−01	1.70031E−01	8.83503E−02	6.11538E−01	1.58184E−01	1.96891E−01
Pu	5.15462E−01	1.74392E−01	9.09214E−02	6.39267E−01	1.61736E−01	2.02720E−01
Am	3.82416E−01	2.21024E−01	1.00203E−01	3.78945E−01	1.32066E−01	2.12494E−01
Cm	5.70664E−01	1.81356E−01	9.65013E−02	4.11512E−01	1.39324E−01	2.17472E−01
Bk	5.87327E−01	1.88945E−01	9.96481E−02	4.16849E−01	1.41019E−01	2.24476E−01
Cf	6.05115E−01	1.96437E−01	1.02802E−01	4.61080E−01	1.48525E−01	2.30876E−01
Es	6.06140E−01	2.07729E−01	1.05988E−01	5.42142E−01	1.60347E−01	2.38280E−01
Fm	6.33782E−01	2.10247E−01	1.11063E−01	3.76456E−01	1.33369E−01	2.41276E−01
Md	6.30207E−01	2.21717E−01	1.14084E−01	4.41196E−01	1.46118E−01	2.48913E−01
No	6.30493E−01	2.32070E−01	1.17753E−01	5.03174E−01	1.56215E−01	2.55229E−01
Lr	6.67683E−01	2.37016E−01	1.26182E−01	3.27481E−01	1.17241E−01	2.51651E−01

Table 10 Exponents of 6s/6p correlating 3d2f1g functions for the quadruple-zeta basis sets

Element	d	d	d	f	f	g
Ac	1.00179E+00	8.81258E−01	3.72221E−01	8.67145E−01	4.04380E−01	7.34557E−01
Th	1.07096E+00	1.07127E+00	4.31650E−01	9.61030E−01	4.48248E−01	8.09473E−01
Pa	9.94208E−01	9.89394E−01	4.03732E−01	9.65320E−01	5.60785E−01	7.98900E−01
U	1.09812E+00	9.78387E−01	4.19355E−01	1.01403E+00	5.75963E−01	8.37125E−01
Np	1.18054E+00	9.89394E−01	4.34295E−01	1.06071E+00	5.91786E−01	8.75163E−01
Pu	1.16556E+00	7.05578E−01	3.08603E−01	1.08465E+00	5.84802E−01	8.44054E−01
Am	1.21958E+00	7.27992E−01	3.18361E−01	1.12863E+00	6.01102E−01	8.78802E−01
Cm	1.49037E+00	9.98448E−01	4.59905E−01	1.11822E+00	5.93841E−01	9.94726E−01
Bk	1.32450E+00	7.70554E−01	3.35794E−01	1.21543E+00	6.35770E−01	9.47342E−01
Cf	1.37743E+00	7.91928E−01	3.44438E−01	1.25887E+00	6.52851E−01	9.82086E−01
Es	1.43094E+00	8.13430E−01	3.53061E−01	1.30261E+00	6.69841E−01	1.01721E+00
Fm	1.48499E+00	8.34972E−01	3.61557E−01	1.34680E+00	6.86899E−01	1.05267E+00
Md	1.53937E+00	8.56472E−01	3.69940E−01	1.39147E+00	7.03989E−01	1.08851E+00
No	1.59491E+00	8.78350E−01	3.78382E−01	1.43683E+00	7.21198E−01	1.12483E+00
Lr	1.83298E+00	1.15502E+00	5.28607E−01	1.50972E+00	7.63622E−01	1.24846E+00

contraction patterns described below. The contracted basis sets are formed by adding primitive functions to the SCF occupied spinor or orbital set. The contractions for the actinides must cover two regions of space: that occupied by the outer valence 6d, 7s, and 7p shells, and that occupied by the inner valence 5f, 6s, and 6p shells.

Table 11 Exponents of 5d correlating 3f2g1h functions for the quadruple-zeta basis sets

Element	f	f	f	g	g	h
Ac	4.48153E+00	2.41414E+00	1.16514E+00	3.76025E+00	1.81990E+00	3.15688E+00
Th	4.73046E+00	2.58545E+00	1.26251E+00	3.97082E+00	1.94840E+00	3.35510E+00
Pa	4.90397E+00	3.47975E+00	1.80718E+00	4.13141E+00	2.00797E+00	3.70744E+00
U	5.06665E+00	3.79972E+00	1.95979E+00	4.32736E+00	2.11191E+00	3.90240E+00
Np	5.20727E+00	4.14093E+00	2.10911E+00	4.52477E+00	2.21530E+00	4.09599E+00
Pu	5.50388E+00	4.14472E+00	2.12632E+00	4.70883E+00	2.29654E+00	4.25902E+00
Am	5.65866E+00	4.47843E+00	2.27327E+00	4.91101E+00	2.40066E+00	4.45447E+00
Cm	5.33896E+00	5.33967E+00	2.52740E+00	5.12851E+00	2.52925E+00	4.52960E+00
Bk	5.88425E+00	5.23661E+00	2.55703E+00	5.32016E+00	2.60772E+00	4.84597E+00
Cf	5.81847E+00	5.80517E+00	2.69405E+00	5.52899E+00	2.71272E+00	5.04397E+00
Es	6.06276E+00	6.06316E+00	2.81336E+00	5.74096E+00	2.81890E+00	5.24368E+00
Fm	6.32106E+00	6.32104E+00	2.93387E+00	5.95578E+00	2.92609E+00	5.44533E+00
Md	6.58427E+00	6.58423E+00	3.05611E+00	6.17366E+00	3.03441E+00	5.64905E+00
No	6.85359E+00	6.85374E+00	3.18046E+00	6.39466E+00	3.14394E+00	5.85500E+00
Lr	7.31787E+00	7.31835E+00	3.39715E+00	6.63471E+00	3.27865E+00	6.08895E+00

Table 12 Exponents of 5f dipole polarizing 1g1h1i functions for the quadruple-zeta basis sets

Element	g	h	i
Pa	7.82108E−02	1.18887E−01	3.03306E−01
U	9.06885E−02	1.43692E−01	3.43197E−01
Np	1.02206E−01	1.69920E−01	3.81529E−01
Pu	9.43673E−02	1.75092E−01	3.75453E−01
Am	1.06109E−01	2.00726E−01	4.35871E−01
Cm	1.27204E−01	2.08291E−01	4.84121E−01
Bk	1.25032E−01	2.19334E−01	5.06616E−01
Cf	1.43830E−01	2.52442E−01	5.61600E−01
Es	1.44987E−01	2.67168E−01	5.82338E−01
Fm	1.56282E−01	2.84473E−01	5.88885E−01
Md	1.65881E−01	3.03697E−01	6.23170E−01
No	1.76068E−01	3.28535E−01	6.59003E−01
Lr	2.55772E−01	4.61190E−01	9.05725E−01

Table 13 Exponents of 6d/7s dipole polarizing 1f1g1h functions for the quadruple-zeta basis sets

Element	f	g	h
Ac	5.58391E−02	7.77918E−02	1.16396E−01
Th	5.04047E−02	4.21407E−02	9.32767E−02
Pa	5.59170E−02	9.96109E−02	1.22713E−01
U	5.45733E−02	8.36807E−02	1.23261E−01
Np	5.80724E−02	1.03974E−01	1.29416E−01
Pu	5.95396E−02	1.05912E−01	1.32751E−01
Am	6.37343E−02	8.40005E−02	1.35157E−01
Cm	5.65089E−02	8.15850E−02	1.27346E−01
Bk	5.55196E−02	7.85696E−02	1.25068E−01
Cf	5.40372E−02	7.80715E−02	1.21359E−01
Es	5.26077E−02	7.95889E−02	1.18272E−01
Fm	5.30666E−02	6.37242E−02	1.15283E−01
Md	5.09507E−02	6.52574E−02	1.11166E−01
No	4.89262E−02	6.49069E−02	1.06047E−01
Lr	4.68390E−02	4.35200E−02	9.34136E−02

These regions overlap to some extent, so that it is not usually possible to define separate contractions. In addition, excitations from the 5d shell can be important, especially 5d → 5f excitations, so that correlation of the 5d shell must be considered for high accuracy.

The contraction pattern is described first for the outer valence shells, then the additional functions required for the inner valence are described, and finally the functions for correlation of the 5d. To any of these contractions, the relevant dipole polarization functions listed in Tables 2, 5, 6, 12 and 13 can be added.

In the descriptions, functions are counted by increasing exponent size, from the smallest. In cases where linear dependence might be a problem, alternative prescriptions are given.

4.1 Double-zeta basis sets

- *Outer valence 6d/7s/7p:* to the SCF functions, add the 2nd s primitive, the 2nd p primitive, the 1st d primitive, and the valence correlating f function.
- *Inner valence 5f/6s/6p:* to the outer valence set, add the 4th s primitive, the 4th p primitive, the 3rd and 4th d primitives, the 1st and 2nd f primitives, and the correlating g function.
- *Core 5d:* to the inner valence set, add the 6th s, p, and d primitives, and the 4th f primitive.

4.2 Triple-zeta basis sets

- *Outer valence 6d/7s/7p:* to the SCF functions, add the 1st and 3rd s primitives, the 2nd and 3rd p primitives, the 1st and 2nd d primitives, the 6d/7s correlating 2f1g functions for Ac, and the 1st and 2nd f primitives and the valence correlating g function for the rest of the block.
- *inner valence 5f/6s/6p:* to the outer valence set, add the 4th and 6th s primitives, the 5th and 6th p primitives, the 3rd and 4th d primitives, the 3rd

through 5th f primitives, and the 5f correlating 2g1h set.
If linear dependence problems are encountered in the f space, do not add the 3rd f primitive.

- *Core 5d:* to the inner valence set, add the 7th and 9th s primitives, the 8th and 9th p primitives, and the 6th and 7th d primitives. The f and g spaces are covered by the inner valence set.

4.3 Quadruple-zeta basis sets

- *Outer valence:* to the SCF functions, add the 1st, 2nd, and 4th s primitives, the 2nd through 4th p primitives, the 1st through 3rd d and f primitives, and the valence correlating 2g1h set.
- *Inner valence:* to the outer valence set add the 5th, 6th, and 8th s primitives, the 6th, 7th and 8th p primitives, the 4th, 5th and 6th d primitives, the 4th f primitive, and the 5f correlating 3g2h1i set.
If linear dependence problems are encountered in the d space, do not include the 2nd d primitive.
- *Core 5d:* to the inner valence set, add the 9th through 11th s and p primitives, the 7th d primitive, and the 5th and 6th f primitives, and for Ac the 5d correlating 2g1h set. The 5d correlating 2g1h set is well enough represented by the 5f correlating functions to be omitted for the rest of the block.

5 Application

As a test of the basis sets, calculations have been performed on the Lr atom, for which the $7s^2\ 6d^1$ and $7s^2\ 7p^1$ configurations are very close. High-level coupled-cluster calculations predict that the $7s^2\ 7p^1_{1/2}\ J = 1/2$ state is the ground state, with the spin–orbit components of the $7s^2\ 6d^1$ between it and the $7s^2\ 7p^1_{3/2}\ J = 3/2$ state [26].

The relative positions of the four states in question are determined by a balance between several contributions: (1) correlation within the reference space of the 6d, 7s, and 7p orbitals (including their spin–orbit components), which is largely nondynamical correlation; (2) internal correlation due to excitations into the reference space from the outer core 6s and 6p orbitals and from the 5f orbital, (3) valence correlation; (4) core-valence correlation, and (5) core–core correlation.

In addition to these effects, there is a dependence of the results on the SCF orbitals used as a basis for the correlated calculations, which may be considered as relaxation effects. Here, there are three main possibilities: (a) common orbitals for both configurations, optimized on the average energy of the two configuration average energies; (b) separate orbitals for both configurations, optimized on the weighted average energy of the spin–orbit components; and (c) separate orbitals for each spin–orbit component.

The current calculations are more modest than the coupled-cluster calculations, but are still sufficiently accurate for the purpose of illustrating the basis sets. In the main set of calculations, the orbitals were generated for the average energy of the two configurations (option (a) above). The spin–orbit components were weighted by their degeneracy, and the configuration weights were selected so that the occupation of the unpaired electron was 0.5 for each configuration. For all three basis sets (dz, tz, and qz), energies were obtained from the DHF calculations, from the reference space CI calculation, then for valence correlation in which single and double excitations from all reference configurations were considered. In addition to the basis set calculations, results were obtained for DHF and reference space CI calculations based on numerical orbitals. The effect of core–valence and core–core correlation for the 6s and 6p outer core shells was assessed with the dz and tz basis sets (the qz basis set was omitted due to size limitations on the CI code). First, valence SDCI calculations were performed with the expanded basis set. Next, internal excitations were added to these SDCI calculations; then single and double excitations were added in which one electron was excited from the 6s or 6p shell; and finally double excitations from the 6s and 6p shells were added.

The valence correlation results are presented in Table 14. The DHF and reference space CI calculations at the qz level are practically identical to the numerical results. There is considerably more variation in the valence SDCI calculations, mainly in the location of the 6d levels. The spin–orbit splitting of both the 7p and the 6d orbital is fairly stable.

In the core–valence correlation studies, whose results are presented in Table 15, it is clear that the addition of the core correlating functions in the valence SDCI calculations has a noticeable effect at the dz level, but little effect at the tz level. This is an indication of the incompleteness of the dz basis sets, which should generally be used for qualitative rather than quantitative studies. Addition of the internal excitations has a noticeable effect, of the order of 200 cm^{-1}. Both core–valence and core–core correlation have a major impact on the position of the 6d energy levels relative to the 7p levels, lowering the 6d level considerably. The effect on the spin–orbit splittings is of the order of 200 cm^{-1}.

Table 14 Excitation energies in cm^{-1} for the 6d and 7p states of Lr, as a function of basis set and valence correlation level

State	Basis	DHF	Ref	Val-SDCI
$6d_{3/2}$	dz	5527	6331	4969
	tz	5559	6378	5174
	qz	5543	6365	4839
	num	5541	6363	
$6d_{5/2}$	dz	7442	8433	7207
	tz	7438	8508	7467
	qz	7413	8487	7058
	num	7409	8484	
$7p_{3/2}$	dz	8065	8488	8112
	tz	8013	8405	8207
	qz	8013	8403	8206
	num	8013	8402	
6d spin–orbit	dz	1915	2157	2238
	tz	1880	2130	2293
	qz	1871	2122	2219
	num	1869	2121	

DHF single-configuration values, *Ref* values from full CI in the reference space (6d, 7s, 7p), *Val-SDCI* values from singles and doubles CI from the reference space

Table 15 Excitation energies in cm^{-1} for the 6d and 7p states of Lr, as a function of basis set and correlation of the 6s and 6p shells: single-configuration values

State	Basis	Val-SDCI	6s6p int	6s6p cv	6s6p core
$6d_{3/2}$	dz	5194	4972	4459	3478
	tz	5155	4909	3298	1814
$6d_{5/2}$	dz	7434	7492	6990	6076
	tz	7455	7481	6160	4778
$7p_{3/2}$	dz	8202	8066	8020	8070
	tz	8209	8066	8212	8251
6d spin–orbit	dz	2240	2520	2532	2598
	tz	2300	2572	2862	2964

Ref values from full CI in the reference space (6d, 7s, 7p), *Val-SDCI* valence singles and doubles CI from the reference space including the 6s6p correlating functions, *6s6p int* internals from the 6s and 6p shell to the reference space added, *6s6p cv* single and double excitations with one electron from the 6s and 6p shells added. *6s6p core* double excitations from the 6s and 6p shells added

Table 16 Orbital dependence of excitation energies in cm^{-1} for the 6d and 7p states of Lr

State	Orbital set	Energy
$6d_{3/2}$	Config av	5541
	Separate configs	5223
	Separate states	5197
$6d_{5/2}$	Config av	7410
	Separate configs	7289
	Separate states	7293
$7p_{3/2}$	Config av	8013
	Separate configs	7777
	Separate states	7797
6d spin–orbit	Config av	1869
	Separate configs	2066
	Separate states	2096

Finally, the orbital dependence was assessed through numerical DHF calculations. Results of these calculations are presented in Table 16. The effect of averaging over both configurations is largest, at about 200–300 cm^{-1}, while the relaxation of the individual spin–orbit components is an order of magnitude smaller.

6 Discussion

The polarizing (diffuse) g functions are important at the SCF level for species such as the actinyls, AnO_2^{n+}, which have an inversion center at the actinide. These g functions contribute to the σ_g and π_g bonding orbitals which have their principal actinide contribution from the 6d orbital. Because of the inversion center, the g functions are the first polarization functions, and serve in particular to bring the charge density from the dπ orbitals closer to the oxygen atoms. The inclusion of g functions in the basis set changes both the bond length and the harmonic frequency at the SCF level for UO_2^{2+}, for example. Polarization of the 5f in the σ_u and π_u bonding orbitals in the actinyls is less important because these orbitals are already more directed towards the oxygen atoms. The addition of h functions does however contribute to the depth of the minimum, even if these functions do not affect the bond length or the frequency much.

The changing nature of the 5f shell across the actinide series forces some compromise in the definition of the basis sets and the contraction patterns. The range of correlating functions for the various shells overlaps somewhat, and the degree of overlap changes across the block. As a consequence, some correlation is lost in the attempt to provide a reasonably uniform basis set composition. This loss might compromise the usefulness of the basis sets for energy extrapolations as is done with nonrelativistic basis sets [31–33], but it remains to be seen how serious the compromise is.

An alternative solution to the optimization of the exponents of a minimum set of primitive functions is to use atomic natural orbital (ANO) contractions [34,35] (or atomic natural spinor contractions, ANSs) of a somewhat larger, but more uniformly distributed, set of primitives. Such contractions would in fact be desirable for the NESC methods [36,37], for which the basis set should be derived from the positive-energy spinors of the relevant Dirac–Hartree–Fock calculations. For these methods, the addition of primitives using a Dirac free-particle approximation is problematic for larger exponents [18].

The trade-off in the use of ANOs or ANSs is in the cost of the primitive integrals for functions of higher angular momentum, but given that the cost of integral evaluation is not the major consideration in highly accurate correlation studies, this cost would not be a serious disadvantage. The range of exponents required can be selected on the basis of the optimization of primitives.

The full tables of basis sets including spin-free relativistic SCF [38] and Dirac–Fock SCF coefficients are available in ASCII format from the Dirac web site, http://dirac.chem.sdu.dk. The spin-free relativistic SCF coefficients include the Foldy–Wouthuysen transformed large component coefficients that can be used in the scalar one-electron NESC approximation [37].

7 Internet archive

This paper includes an internet archive in ASCII format. The archive contains the Dirac–Fock SCF coefficients and the spin-free relativistic SCF coefficients, including the Foldy–Wouthuysen transformed large component coefficients, and the correlating and polarizing functions. Prescriptions are given in the archive for the construction of various basis sets.

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