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REGULAR ARTICLE

Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 6d elements Rf–Cn

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Abstract Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized for the 6d elements Rf–Cn. The basis sets include SCF exponents for the occupied spinors and for the 7p shell; exponents of correlating functions for the valence shell, the 6s and 6p shells, and the 5f shell; and exponents of functions for dipole polarization of the 6d shell. A finite nuclear size was used in all optimizations. Prescriptions are given for constructing contracted basis sets. The use of the basis sets is demonstrated for some atomic and molecular systems. The basis sets are available as an Internet archive and from the Dirac program Web site, http://dirac.chem.sdu.dk.

Keywords Relativistic basis set · 6d elements · Gaussian functions · Double-zeta · Triple-zeta · Quadruple-zeta · Correlating functions

1 Introduction

There is a significant interest in the 6d transition elements, all of which have short half-lives and can be produced only a few atoms at a time [1]. Despite the enormous challenges, some chemical properties of these elements have been measured. But because of these challenges, theoretical predictions have an important place in the design and analysis of the experiments [1–3]. Since inclusion of relativistic effects in calculations on these elements is mandatory, basis sets for such calculations are needed.

The electronic structure of the 6d block elements is strongly affected by relativity. Due to the relativistic contraction of the 7s shell and the expansion of the 6d shell, the 7s is doubly occupied in the ground states of all the neutral elements [4], and further, the 7s spinor energy is more negative than the spinor energies of both spin-orbit components of the 6d shell. At the beginning of the block, for Lr, the $7p_{1/2}$ spinor is stabilized enough by spin-orbit effects that the ground state configuration is $7s^27p^1$ rather than $6d^17s^2$, and for Rf, the $6d^17s^27p^1$ configuration competes with the $6d^27s^2$ configuration for the ground state [5]. DHF calculations show that the $6d^{n-1}7s^27p^1$ configuration is within about 0.1 eV of the $6d^n7s^2$ configuration for Rf, Db, Hs, and Mt and is always lower than the $6d^{n+1}7s^1$ configuration.

In this paper, relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 6d elements Rf–Cn are presented. These basis sets are part of an ongoing effort [6–15] to provide basis sets for all-electron relativistic calculations, in the style of the correlation-consistent basis sets [16–19], that give fairly uniform quality across the lower portion of the periodic table. In addition to the SCF sets, which include functions to describe the 7p shell, the basis sets include high angular momentum correlating functions for the 6d shell, the 6s and 6p shells, and the 5f shell, and functions for dipole polarization of the 6d shell. Prescriptions for the selection of primitive functions for basis set flexibility and electron correlation are provided, and the use of the basis sets is illustrated in some atomic and molecular calculations.

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birth day and published as part of the Pyykkö Festschrift Issue.

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2 Methods

The methods used have been described previously [6, 8, 20, 21]. The basis sets were optimized in Dirac-Hartree-Fock calculations using the Dirac-Coulomb Hamiltonian with the standard Gaussian nuclear charge distribution [22]. As for the previous basis sets, ℓ-optimization was employed. The configuration used for the optimization of the occupied spinors was the $6d^n7s^2$ configuration, as this is the ground configuration for all the elements in the series. Experience with the 5d block [14] suggests that the choice of configuration is not critical, however. For the 7p spinors, functions were added to the p set: 2 for dz, 3 for tz, and 4 for qz. These functions were optimized on the $6d^{n\text{-}1}7s^27p^1$ configuration, along with reoptimization of the p functions for all except the 2p spinor.

Correlating functions were optimized in MR-SDCI calculations on the ground configuration, using the RAMCI program [21] modified for basis set optimization. All states of this configuration, weighted by their J value, were included in the optimization. This reference set was used in all correlating function optimizations.

For the valence 6d and 7s shells, the correlating function spaces were 1f for the dz basis set, 2f1g for the tz basis set and 3f2g1h for the qz basis set. All single and double excitations out of the 6d and 7s orbitals were included in the CI expansion. Additional functions for correlation of the 6s and 6p shells are not needed, because they are covered by the functions for the other shells. For the 5f shell, the correlating function spaces were 1g for the dz basis set, 2g1h for the tz basis set, and 3g2h1i for the qz basis sets. All single and double excitations from the 5f shell that couple to $J = 0$ were included in the CI expansion. The correlating function spaces also correspond to the primitives added for correlation. Each primitive provided a single 4-spinor with the coefficients of the large and small components derived by diagonalizing the free-particle Dirac Hamiltonian for the primitive in question. The 4-spinors were then orthogonalized for the CI calculations.

Functions for dipole polarization of the 6d shell were determined as follows. For the dz basis sets, a single f function was determined 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. The ratio of the polarizing f exponent to the correlating f exponent for the dz sets was applied to the outermost exponents of the correlating sets for the tz and qz basis sets to obtain a 1f1g set and a 1f1g1h set, respectively.

Due to the low-lying 7p configurations, the basis sets were contracted for the average of the four configurations $6d^n7s^2$, $6d^{n+1}7s^1$, $6d^n7s^17p^1$, and $6d^{n\text{-}1}7s^27p^1$, with equal weights. This resulted in an effective configuration of $6d^n7s^{1.5}7p^{0.5}$.

Contracted basis sets are formed in the same way as for the correlation-consistent basis sets [16–19], with the SCF occupied orbitals forming a generally contracted set, and the addition of primitive functions for correlation. For the lower occupied symmetries, these primitives are taken from the SCF set. To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed on Rf and Cn, 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 6d/7s correlation in the tz basis sets, the correlating set was 2s2p3d2f1g. 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.

The selection of primitives that gave the lowest energy was chosen, in most cases, to determine the contraction pattern. Where there was a difference between the calculations for Rf and for Cn, a compromise that gave the smallest error for either element was chosen. This procedure was used for 6d7s correlation, 6s6p correlation, and 5f correlation independently. There is overlap between the sets of primitives thus determined, so the recommendations for contraction are for successive inclusion of spinors in the basis sets, with only the nonredundant exponents being added for each inclusion.

Sample atomic calculations were performed with the GRASP [20, 24] and RAMCI [21] programs. The coefficient of fractional parentage (CFP) package in RAMCI was supplemented for $j = 9/2$, 11/2, and 13/2 to allow the use of higher than double excitations with high angular momentum functions.

Sample molecular calculations were performed with the DREAMS package.[1] In these calculations, integrals of the type SSSS were included only for the occupied spinors of the atoms (which form the set of contracted functions in the basis set). SCF calculations were performed with the full molecular symmetry, followed by MP2 calculations. Open-shell MP2 calculations included a denominator shift [27]. For diatomics, calculations were performed on the atoms in the full molecular basis, to produce counterpoise-corrected potential energy curves. For the polyatomics, calculations

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[1] DREAMS is a Dirac-based Relativistic Electronic Atomic and Molecular Structure program suite, consisting of an adapted version of MOLECULE, a vectorized integral program developed by J. Almlöf and P. R. Taylor, and a Dirac-Hartree-Fock and MP2 program developed by Dyall. The DHF program methods are described in [25] and the MP2 program methods are described in [26].

were performed on the metal atoms in the full molecular basis, and the counterpoise correction for the other atoms was taken from the calculations in the diatomic basis, following the ideas of Jensen [28]. The points on the potential curves were spaced at 5pm in the bonding coordinate, and the bond length, dissociation energy, and harmonic frequency were obtained from a quartic fit to seven points around the minimum.

3 Primitive basis sets

The initial basis set sizes were selected for consistency with the 5f basis sets [12], which were 26s21p17d10f for the dz basis sets, 33s26p20d12f for the tz basis sets, and 37s31p24d14f for the qz basis sets. For the dz basis sets, the 6d spinor had a marginal qz exponent set, so the size of the d set was reduced to 16d. This is consistent with the changes from the 4f block to the 5d block, where the number of d functions was reduced because the multiply occupied d shell is more compact [15]. For the tz and qz basis sets, it was difficult to optimize the s sets with the same sizes as in the 5f block. This is because the nuclear radius is increasing and pushing the s distribution out. At the same time, the increased nuclear charge is pulling the orbitals in. It was therefore found necessary to reduce the sizes of the s sets, to 32s for the tz basis sets and 36s for the qz basis sets. No further changes in the sizes were needed, so the SCF sets used in the optimizations were 26s21p16d10f for the dz basis sets, 32s26p20d12f for the tz basis sets, and 36s31p24d14f for the qz basis sets. With the addition of the functions for the 7p, the final basis set sizes are 26s23p16d10f (dz), 32s29p20d12f (tz), and 36s35p24d14f (qz).

The nuclear mass used is intended to be that of the most stable isotope. However, since the discovery of isotopes of these elements is continuing, it is possible that the most stable isotope has not yet been discovered. The original sets used the most stable isotopes at the time of generation, but since then more stable isotopes have been discovered in most cases. The SCF s and p sets were therefore reoptimized with the newer isotopes. The changes are mostly in the core, with very small valence changes. As the basis set size increases, there is tighter coupling between the exponents, and the valence exponents change more. The changes are still only of the order of one percent, which is not enough to affect results for valence properties.

Configuration average total energies for the ground d^ns^2 configuration from calculations using these basis sets (for all isotopes considered), uncontracted, are compared with the numerical values in Table 1. The energies of the tz and the qz basis sets are lower than the numerical energies, due to the fact that the exact Dirac-Hartree-Fock energy is not a lower bound to approximate energies. With kinetic balance (which is used here), the energy can be below the exact energy by at most order c^{-4}, a phenomenon known as prolapse [23].

Configuration average total DHF energies from calculations using the uncontracted SCF basis sets for the average of the d^ns^2 and $d^ns^1p^1$ configurations, weighted

Table 1 Configuration average Dirac-Hartree-Fock total energies in E_h for uncontracted basis set calculations on the ground configurations, d^ns^2

Element	Isotope	Double-zeta	Triple-zeta	Quadruple-zeta	Numeric
Rf	263	−38,693.747549	−38,693.772409	−38,693.773668	−38,693.767132
	265*	−38,693.560316	−38,693.585160	−38,693.586412	−38,693.579862
Db	262	−39,699.522052	−39,699.546624	−39,699.547766	−39,699.540471
	268*	−39,698.904815	−39,698.929309	−39,698.930397	−39,698.923091
Sg	266	−40,724.921836	−40,724.946546	−40,724.947662	−40,724.939447
	272*	−40,724.247908	−40,724.272530	−40,724.273587	−40,724.265361
Bh	272	−41,770.667763	−41,770.692926	−41,770.694038	−41,770.684762
	273*	−41,770.544951	−41,770.570094	−41,770.571204	−41,770.561917
Hs	276*	−42,837.751486	−42,837.777349	−42,837.778462	−42,837.768026
	277	−42,837.617293	−42,837.643139	−42,837.644254	−42,837.633803
Mt	276	−43,927.086542	−43,927.113349	−43,927.114477	−43,927.102793
	279*	−43,926.643561	−43,926.670311	−43,926.671419	−43,926.659711
Ds	278*	−45,038.451868	−45,038.479722	−45,038.480845	−45,038.467761
	281	−45,037.965331	−45,037.993125	−45,037.994267	−45,037.981116
Rg	280	−46,172.736575	−46,172.765599	−46,172.766763	−46,172.752068
	283*	−46,172.201994	−46,172.230955	−46,172.232093	−46,172.217370
Cn	285	−47,330.008351	−47,330.038594	−47,330.039774	−47,330.023248

The more stable isotope is labeled with an asterisk

Table 2 Configuration average total Dirac-Hartree-Fock energies in E_{h} for uncontracted basis set calculations on the weighted average of configurations used for the basis set contractions

Element	Isotope	Double-zeta	Triple-zeta	Quadruple-zeta
Rf	263	−38,693.681723	−38,693.707308	−38,693.708570
	265*	−38,693.494496	−38,693.520061	−38,693.521317
Db	262	−39,699.447603	−39,699.472885	−39,699.474031
	268*	−39,698.830374	−39,698.855579	−39,698.856671
Sg	266	−40,724.838923	−40,724.864341	−40,724.865463
	272*	−40,724.165012	−40,724.190336	−40,724.191400
Bh	272	−41,770.501211	−41,770.602251	−41,770.603372
	273*	−41,770.378404	−41,770.479422	−41,770.480539
Hs	276*	−42,837.651479	−42,837.678081	−42,837.679204
	277	−42,837.517290	−42,837.543874	−42,837.544998
Mt	276	−43,926.977696	−43,927.005275	−43,927.006415
	279*	−43,926.534727	−43,926.562246	−43,926.563366
Ds	278	−45,038.333913	−45,038.362575	−45,038.363712
	281*	−45,037.847389	−45,037.875989	−45,037.877145
Rg	280	−46,172.609170	−46,172.639047	−46,172.640225
	283*	−46,172.074602	−46,172.104416	−46,172.105568
Cn	285	−47,329.871119	−47,329.902261	−47,329.903456

The more stable isotope is labeled with an asterisk

according to the procedure described above, are given in Table 2. The calculations that generated these energies were used to provide DHF contraction coefficients. These energies are provided as reference energies for the contracted basis sets.

4 Contraction patterns

The MR-SDCI calculations that were performed to determine which functions to uncontract yielded the contraction patterns described below. The contracted basis sets are formed by taking the SCF occupied spinors or orbitals as generally contracted functions, and adding primitive functions for valence correlation and flexibility. Three primary contraction patterns are described, for a valence basis set, which correlates the 6d and 7s shells; a valence + outer core set, which adds functions for 6s and 6p correlation to the valence set, and a valence + outer core + 5f set, which adds functions for 5f (and other $n = 5$ subshells) to the valence+outer core set. To any of these contractions, the relevant dipole polarization functions can be added. These functions have a similar mean radius to the outermost d function; the outermost s function and p function are more diffuse. If a diffuse d or s function is needed, an even-tempered extension of the SCF set should be adequate; the outermost p function is already quite diffuse.

The contraction patterns include an extra d function—the outermost—in the valence space, because flexibility of the d orbital is critical in transition metal complexes. However, if linear dependence is encountered in the d space, the outermost d function should not be uncontracted. The SCF set includes the 7p function, although it is not formally occupied.

In the descriptions, functions are counted by increasing exponent size, from the smallest. The valence correlating f functions are included in the SCF sets.

4.1 Double-zeta basis sets

- **Valence:** To the SCF functions, add the 2nd s and p primitives, the 1st and 2nd d primitives, and the valence correlating *f* function (included in the contraction). Basis set size: 8s7p6d3f.
- **Valence + 6s6p:** To the valence set, add the 4th s primitive, the 3rd p primitive, and the 3rd d primitive. Basis set size: 9s8p7d3f.
- **Valence + 6s6p + 5f:** To the valence + 6s6p set, add the 4th d primitive, the 2nd f primitive, and the 5f correlating g function. Basis set size: 9s8p8d4f1g.

4.2 Triple-zeta basis sets

- **Valence:** To the SCF functions, add the 1st and 3rd s primitives, the 2nd and 3rd p primitives, the 1st through 3rd d primitives, and the valence correlating 2f1g functions. Basis set size: 9s8p7d4f1g.
- **Valence + 6s6p:** To the valence set, add the 4th and 6th s primitives, the 5th and 6th p primitives, the 4th and 5th d primitives, and the 3rd f function. Basis set size: 11s10p9d5f1g.
- **Valence + 6s6p + 5f:** To the valence + 6s6p set, add the 4th f primitive, and the 5f correlating 2g1h functions. Basis set size: 11s10p9d6f3g1h.

4.3 Quadruple-zeta basis sets

- **Valence:** To the SCF functions, add the 2nd through 4th s primitives, the 2nd through 4th p primitives, the 1st through 4th d primitives, and the valence correlating 3f2g1h set. Basis set size: 10s9p8d5f2g1h.
- **Valence + 6s6p:** To the valence set add the 5th, 6th, and 8th s primitives, the 5th, 7th, and 8th p primitives, the 5th and 6th d primitives, and the 4th f primitive. Basis set size: 13s12p10d6f2g1h.
- **Valence + 6s6p + 5f:** To the valence + 6s6p set, add the 7th d primitive, the 5th f primitive, and the 5f correlating 3g2h1i functions. Basis set size: 13s12p11d7f5g3h1i.

5 Applications

Several applications have been chosen to demonstrate the use of the basis sets developed in this work. These applications seek to highlight some of the differences between the 6d block and the lower blocks and to illustrate the effects of relativity.

5.1 Atomic calculations

The first set of calculations was designed to explore the relative positioning of the $6d^n7s^2$, $6d^{n+1}7s^1$, and $6d^{n+2}$ configurations. MR-SDCI calculations were carried out on the neutral atoms and the singly, doubly, and triply charged ions. The reference space included the 6d and 7s spinors, with all possible occupations.

The first three ionization potentials are reported in Table 3, along with the identity of the spinor that is ionized. As others have noted, the first electron to be removed comes from the 6d orbital across the row, which means that the ground state comes from the $6d^n7s^2$ configuration for both the neutral atom and the 1+ ion. The trend in the first IP follows the pattern expected for *jj* coupling: the IP increases until Sg, at which point the $6d_{3/2}$ shell is filled, and the IP drops for Bh, for which the filling of the $6d_{5/2}$ shell commences. From Mt to Ds, there is a smaller increase in the first IP, which might be ascribed to the fact that Mt has a half-filled $6d_{5/2}$ shell.

For the second IP, the electron also comes from the 6d for Rf, Db, Mt, and Ds. Bh^+ has a filled $6d_{3/2}$ shell, and so removal of the electron from the 7s is expected. Hs^+ has a $6d_{3/2}^4 6d_{5/2}^1 7s^2$ configuration, and one might expect the $6d_{5/2}$ electron to be removed, but it is the 7s electron, presumably due to the 7s repulsion. The general pattern is the increasing stabilization of the d spinors with respect to the s, so that the 7s is lost in the latter part of the block.

Table 3 First three ionization potentials (in eV) of the 6d elements as a function of basis set size, from MR-SDCI calculations

Element	Basis	IP1	IP2	IP3
Rf	dz	5.607 (6d)	13.695 (6d)	22.989 (7s)
	tz	5.702 (6d)	13.761 (6d)	22.967 (7s)
	qz	5.729 (6d)	13.775 (6d)	22.942 (7s)
Db	dz	6.495 (6d)	15.145 (6d)	23.981 (7s)
	tz	6.576 (6d)	15.251 (6d)	24.024 (7s)
	qz	6.610 (6d)	15.260 (6d)	24.003 (7s)
Sg	dz	7.503 (6d)	16.269 (7s)	24.946 (7s)
	tz	7.594 (6d)	16.388 (7s)	25.003 (7s)
	qz	7.642 (6d)	16.385 (7s)	24.993 (7s)
Bh	dz	7.333 (6d)	17.024 (7s)	26.088 (7s)
	tz	7.410 (6d)	17.175 (7s)	26.159 (7s)
	qz	7.465 (6d)	17.180 (7s)	26.140 (7s)
Hs	dz	7.412 (6d)	17.259 (7s)	27.517 (6d)
	tz	7.613 (6d)	17.491 (7s)	27.551 (6d)
	qz	7.708 (6d)	17.463 (7s)	27.558 (6d)
Mt	dz	8.563 (6d)	17.976 (6d)	27.809 (7s)
	tz	8.726 (6d)	18.192 (6d)	28.059 (7s)
	qz	8.822 (6d)	18.248 (6d)	28.025 (7s)
Ds	dz	9.143 (6d)	19.201 (6d)	29.251 (7s)
	tz	9.307 (6d)	19.378 (6d)	29.448 (7s)
	qz	9.400 (6d)	19.434 (6d)	29.494 (7s)
Rg	dz	10.012 (6d)	20.428 (7s)	30.249 (6d)
	tz	10.194 (6d)	20.583 (7s)	30.389 (6d)
	qz	10.283 (6d)	20.651 (7s)	30.451 (6d)
Cn	dz	11.568 (6d)	21.768 (7s)	31.243 (7s)
	tz	11.687 (6d)	21.896 (7s)	31.388 (7s)
	qz	11.779 (6d)	21.890 (7s)	31.400 (7s)

The shell from which the electron is removed is given in parentheses

For the third IP, the 7s is ionized for all except Hs and Rg. For Bh^{2+}, the filled $6d_{3/2}$ shell can be invoked as an explanation for ionization from the 7s. For Hs^{2+}, it is a choice between a single electron in the 7s shell and a single electron in the $6d_{5/2}$ shell, and the latter is the one that is ionized. For Db, the third ionization is not a simple removal of an electron from a single spinor, because the ground state of Db^{3+} is $6d_{3/2}^2$, so the process is a two-electron process in which a 7s electron is removed and the other 7s electron is transferred into the $6d_{3/2}$.

Which electron is ionized is of course determined by the relative energies of the states of the three configurations, $6d^n7s^2$, $6d^{n+1}7s^1$, and $6d^{n+2}$. The energies of the $6d^{n+1}7s^1$ and $6d^{n+2}$ configurations relative to the $6d^n7s^2$ for the four ionization states are reported in Tables 4 and 5, along with the J value for the state. Note that the 7s couples to the lower *J* value when coupling to the $6d_{3/2}$ shell. In general, as the charge increases, the states with lower 7s population become more stable. However, because the 7s and the 6d

Table 4 Energies (in eV) of the lowest state of the $6d^{n+1}7s^1$ configuration relative to the $6d^n7s^2$ configuration as a function of ionization state and basis set

Element	Basis	Neutral		1+		2+		3+	
		E	*J*	*E*	*J*	*E*	*J*	*E*	*J*
Rf	dz	2.580	1	2.003	3/2	1.140	1		
	tz	2.583	1	1.973	3/2	1.116	1		
	qz	2.587	1	1.951	3/2	1.088	1		
Db	dz	2.412	1/2	1.507	1	0.537	3/2	−0.776	1
	tz	2.423	1/2	1.519	1	0.513	3/2	−0.721	1
	qz	2.413	1/2	1.499	1	0.499	3/2	−0.708	1
Sg	dz	2.213	3	0.681	1/2	−0.154	1	−1.681	3/2
	tz	2.264	3	0.711	1/2	−0.139	1	−1.652	3/2
	qz	2.259	3	0.695	1/2	−0.159	1	−1.663	3/2
Bh	dz	3.028	9/2	1.055	3	−0.862	1/2	−2.357	1
	tz	2.912	9/2	1.156	3	−0.838	1/2	−2.297	1
	qz	2.864	9/2	1.139	3	−0.872	1/2	−2.318	1
Hs	dz	2.866	5	1.816	9/2	−0.275	3	−2.851	1/2
	tz	2.784	5	1.762	9/2	−0.161	3	−2.793	1/2
	qz	2.717	5	1.678	9/2	−0.237	3	−2.808	1/2
Mt	dz	3.150	9/2	1.434	5	0.370	9/2	−1.281	3
	tz	3.042	9/2	1.403	5	0.344	9/2	−1.147	3
	qz	2.961	9/2	1.320	5	0.266	9/2	−1.150	3
Ds	dz	3.246	3	1.699	9/2	0.193	5	−2.814	9/2
	tz	3.095	3	1.645	9/2	0.189	5	−2.777	9/2
	qz	3.028	3	1.586	9/2	0.162	5	−2.800	9/2
Rg	dz	2.813	1/2	1.777	3	−0.192	9/2	−2.671	2
	tz	2.697	1/2	1.672	3	−0.158	9/2	−2.717	2
	qz	2.645	1/2	1.626	3	−0.169	9/2	−2.752	2
Cn	dz			1.261	1/2	−0.002	2	−2.081	9/2
	tz			1.198	1/2	−0.067	2	−2.092	9/2
	qz			1.102	1/2	−0.124	3	−2.195	9/2

Table 5 Energies (in eV) of the lowest state of the $6d^{n+2}$ configuration relative to the $6d^n7s^2$ configuration as a function of ionization state and basis set

Element	Basis	Neutral		1+		2+		3+	
		E	*J*	*E*	*J*	*E*	*J*	*E*	*J*
Rf	dz	6.815	0	5.302	3/2	3.048	2		
	tz	6.652	0	5.265	3/2	3.006	2		
	qz	6.731	0	5.241	3/2	2.971	2		
Db	dz	8.421	11/2	5.117	0	2.079	3/2	−1.213	2
	tz	6.864	5/2	5.090	0	2.037	3/2	−1.130	2
	qz	6.832	5/2	5.054	0	2.018	3/2	−1.130	2
Sg	dz	8.434	4	4.759	5/2	1.792	0	−2.161	3/2
	tz	8.239	4	4.742	5/2	1.787	0	−2.140	3/2
	qz	8.157	4	4.695	5/2	1.779	0	−2.175	3/2
Bh	dz	9.733	5/2	6.860	0	1.236	5/2	−3.221	0
	tz	9.373	3/2	6.750	0	1.245	5/2	−3.174	0
	qz	9.244	3/2	6.671	0	1.205	5/2	−3.223	0
Hs	dz	8.935	4	7.063	3/2	4.183	2	−2.282	5/2
	tz	8.622	4	7.848	5/2	4.901	3	−2.215	5/2
	qz	8.472	4	7.714	5/2	4.809	3	−2.284	5/2
Mt	dz	9.059	5/2	8.559	0	2.641	9/2	0.151	4
	tz	8.731	5/2	8.319	3	2.533	9/2	0.065	2
	qz	8.577	5/2	8.175	0	2.415	9/2	0.010	2
Ds	dz	8.429	0	5.697	5/2	2.507	4	−1.795	9/2
	tz	8.163	0	5.494	5/2	2.425	4	−1.975	3/2
	qz	8.061	0	5.399	5/2	2.384	4	−2.032	3/2
Rg	dz			4.701	0	2.698	5/2	−2.117	4
	tz			4.497	0	2.587	5/2	−2.193	4
	qz			4.421	0	2.545	5/2	−2.254	4
Cn	dz					0.631	0	−2.410	5/2
	tz					0.492	0	−2.521	5/2
	qz					0.203	0	−2.684	5/2

spinors are so close in energy, the anomalies are probably largely due to subtle changes in screening. The crossing between the lowest $6d^n7s^2$ and $6d^{n+1}7s^1$ states occurs at around the 2+ charge state: for some elements the former is higher, while for others the latter is higher. The crossing between the lowest $6d^{n+1}7s^1$ and $6d^{n+2}$ states occurs at around the 3+ charge state, and again, for some elements the former is higher, while for others the latter is higher. Strong mixing occurs in some cases, leading to anomalous J values, such as for Rg^{3+}, where the $J = 2$ state of the $6d^77s^1$ configuration is lower than the expected $J = 5$ state. This state has an almost equal mix of the $6d^77s^1$ configuration and the $6d^8$ configuration. Likewise for Cn^{2+}, the $6d^97s^1$ and $6d^87s^2$ configurations are strongly mixed in the $J = 2$ state, which is very close to the fairly pure $6d^97s^1$ $J = 3$ state. The latter is the lowest in the qz basis calculations, but only by about 0.05 eV. The coupled-cluster calculations of Eliav et al. [29] place the $6d^87s^2$ $J = 4$ state as the ground state of the double ion, but with the $6d^87s^2$ $J = 2$ and the $6d^97s^1$ $J = 3$ states within a few tenths of an eV.

There are more anomalies in the $6d^{n+2}$ states, because these are mostly highly excited states and can mix strongly with states of the other configuration. In the neutral atoms, they are even above the ionization limit for most of the 6d block.

The values given here represent only a small part of the data generated, which includes energies for all states of the three valence configurations. The full set of energies from the MRCI calculations is available as an Internet archive.

Some tests of the dependence of the results on the SCF configuration were performed for a few elements, with the triple-zeta basis set. The results are presented in Table 6. Ds^{2+} is a case where the ground state is a strong mix of the two configurations; Bh is a case that has significant mixing for the $6d^{n+1}7s^1$; while for Hs, both states are dominated by

Table 6 Dependence of the MR-CISD energy (in eV) of the lowest state of the $6d^{n+1}7s^1$ configuration relative to that of the $6d^n7s^2$ configuration as a function of the SCF configuration used to generate the spinors

SCF configuration	Bh	Hs	Ds^{2+}
$6d^n7s^2$	2.935	2.827	0.212
$6d^{n+1}7s^1$	2.886	2.743	0.173
average	2.912	2.784	0.189

Table 7 Dependence of the first ionization potential in eV of Rf on the basis and level of correlation

Basis	SD	SDT	SDTQ
dz	5.607	5.640	5.653
tz	5.702	5.753	5.769
qz	5.729	5.782	–

the main configuration. The dependence amounts to a few hundredths of an eV. The value for the average configuration lies between the other two, and it can be argued that this represents a fairly unbiased value.

Rf has few enough electrons that calculations beyond MR-SDCI are feasible. The first ionization potential from MR-SDCI, MR-SDTCI, and MR-SDTQCI calculations is given in Table 7 as a function of basis set size. Triple excitations increase the ionization potential by about 0.05 eV, and quadruples by less than 0.02 eV. Calculations on the Au and the Hg first ionization potential in the tz basis also showed that triple excitations added about 0.05 eV to the ionization potential.

The current results can be compared with the highly accurate Fock-space coupled-cluster results of Eliav et al. for Rf [31], Rg [32], and Cn [29]. For Rf, the first two ionization potentials from these authors are 6.01 and 14.37 eV, compared with 5.73 and 13.78 eV from the present work in the qz basis set. The first ionization potential of Rg predicted by these authors is 10.57 eV, compared with 10.28 eV from the present work in the qz basis set. Likewise for Cn, the first two ionization potentials are 11.99 and 22.46 eV, compared with 11.78 and 21.89 eV from the present work. Taking these results as the limit, the present first ionization potentials are about 0.2–0.3 eV too low. Extrapolation of the present results to the basis set limit and inclusion of higher excitations in the valence space would make up about 0.1 eV of this difference.

Johnson et al. have also performed CAS-MCDF calculations for Rf, Sg, Bh, and Hs [30, 33, 34]. Their results are somewhat smaller than the current results, which is explained by the lack of dynamic correlation. They show a decrease in the first ionization potential from Bh to Hs, which is a little surprising, in light of the present results. Their estimated experimental ionization potentials are somewhat larger than the values of Eliav et al. for Rf. If the errors in the present results behave fairly smoothly with Z, their estimates for Sg and Bh are probably correct, but their estimate for Hs would be somewhat too low. It is not clear what the origin of this discrepancy is. Their estimates are listed in Table 8 along with the values of Eliav et al. [29, 31, 32] and estimates from this work obtained by adding 0.3 eV to the qz MR-CISD values. If the coupled-cluster results are also an underestimate, a further increment would be required to reach the actual values.

Table 8 Estimated first ionization potentials of the 6d elements, in eV

Element	Present work	Johnson et al. [30, 33, 34]	Eliav et al. [29, 31, 32]
Rf	6.0	6.5	6.0
Db	6.9		
Sg	7.9	7.9	
Bh	7.7	7.7	
Hs	8.0	7.6	
Mt	9.1		
Ds	9.7		
Rg	10.5		10.6
Cn	12.1		12.0

The calculations so far only take into account the states of even parity. For Rf at least, the $7p_{1/2}$ is low-lying, and the odd parity $6d^1_{3/2}7s^2_{1/2}7p^1_{1/2}$ $J = 2$ state is lower at the DHF level than the even parity $6d^2_{3/2}7s^2_{1/2}$ $J = 2$ state. CAS-MCDF calculations with the 6d, 7s, and 7p spinors in the active space [30] also place the odd parity state lower, by 0.24 eV. The lower energy of the odd parity state can be ascribed to the decrease in repulsion when an electron is promoted from the doubly occupied $6d_{3/2}$ shell to the empty $7p_{1/2}$ shell. However, this promotion also decreases the correlation energy, and inclusion of dynamic correlation should lower the even parity state. In highly accurate coupled-cluster calculations [31], dynamic correlation does indeed lower the even parity state below the odd parity state, by 0.27 eV.

Calculations on neutral Rf have been carried out to examine the behavior of these two states. The spinors were generated for the average configuration with the effective occupation $6d^27s^{1.5}7p^{0.5}$, which represents a compromise between the two states (and is also the configuration used for the contraction of the basis sets). CAS-CI calculations with the 6d, 7s, and 7p spinors in the active space were performed in the dz, tz, and qz basis sets, followed by CI calculations for dynamic correlation with single and double excitations into the correlating space. Results are presented in Table 9. The CAS-CI separation is larger than the

Table 9 Dependence of the energy (in eV) of the $6d^2_{3/2}7s^2_{1/2}$ $J = 2$ state relative to the $6d^1_{3/2}7s^2_{1/2}7p^1_{1/2}$ $J = 2$ state on the basis set and correlation level

Correlation level	dz	tz	qz
CAS-CI	0.529	0.567	0.568
+SD	0.142	0.104	0.085

A positive value means that the first state is higher

0.24 eV obtained by Johnson et al. [30] in CAS-MCDF calculations, but this is probably due to the use of a common set of spinors, so some relaxation is missing. Separate EAL-MCDF calculations on the two configurations followed by CI calculations within the configuration give an energy difference of only 0.09 eV. The lack of relaxation is made up in part by the single excitations in the SD CI calculation, which also adds dynamic correlation. The results given here show that valence correlation alone is insufficient to lower the $6d^27s^2$ below the $6d^17s^27p^1$ state, although it reduces the gap to less than 0.1 eV. The orbital dependence of the energies is almost nonexistent in the qz basis set, so the results at this level are not due to orbital bias. While it is possible that higher excitations (not included here) could lower the $6d^27s^2$ state more, it is unlikely to make a large enough difference to make this state the ground state. Core correlation is therefore needed, in agreement with the findings of Eliav et al. [31].

The lowest odd parity $6d^{n\text{-}1}7s^27p^1$ state is very low-lying for the neutral species in elements other than Rf: for Hs, it is within 0.04 eV of the lowest $6d^n7s^2$ state, from relaxed DHF-CI calculations on these two configurations. Because of differential correlation, it is unlikely to be the ground state, but it may nevertheless be important in the bonding of the 6d elements.

5.2 Molecular calculations

The traditional testing ground for relativistic effects in molecules has been the coinage metal hydrides, CuH, AgH, and AuH, and there have been several calculations on RgH [35–40]. Here, calculations have been carried out for AgH, AuH, and RgH with the basis sets in this work for Rg and those in previous work [9, 11] for Ag and Au, and the correlation-consistent basis sets of Dunning [16] for H. For Ag and Au, the unpaired electron was placed in a spinor of $e_{1/2g}$ symmetry; for Rg, the unpaired electron was placed in a spinor of $e_{5/2g}$ symmetry. These choices reflect the different ground state symmetries. Results are given in Table 10.

To test whether diffuse functions are needed, calculations on RgH were carried out with diffuse functions on H (aug-cc-pvnz), with dipole polarizing functions on Rg, and with both the Rg and H basis sets augmented in this way. The results are presented in Table 11. Diffuse functions made very little difference to the bond lengths. At the SCF level, diffuse functions change the dissociation energy by at most 12 meV (1.1 kJ/mol), which is fairly small. The frequencies change by up to about 20 cm^{-1} for the dz basis, and less than 10 cm^{-1} for the tz and qz basis sets, which is within the error of the fit for the frequencies. At the MP2 level, the dissociation energy changes are up to 0.1 eV in the dz basis for the addition of diffuse functions on Rg, but are an order of magnitude smaller for the larger basis sets. Likewise, there is a variation of 10–20 cm^{-1} in the frequencies, which is fairly small and not much outside the numerical accuracy. So for calculations with the dz basis set, diffuse functions are probably advisable, but are not so important for the larger basis sets.

Table 10 Bond length, dissociation energy, and vibrational frequency of coinage metal hydrides as a function of basis set size

Molecule	Basis	SCF			MP2		
		r_e/pm	D_e/eV	ω_e/cm^{-1}	r_e/pm	D_e/eV	ω_e/cm^{-1}
AgH	dz	169.9	1.183	1,606	163.2	1.924	1,731
	tz	169.8	1.229	1,607	160.4	2.108	1,813
	qz	169.9	1.248	1,604	159.4	2.194	1,848
	extrap	169.9	1.273	1,601	158.0	2.314	1,902
	expt				161.8	2.39	1,760
AuH	dz	157.0	1.749	2,099	152.0	2.740	2,327
	tz	156.7	1.793	2,098	150.7	2.959	2,399
	qz	156.7	1.807	2,103	150.4	3.027	2,406
	extrap	156.6	1.826	2,109	150.1	3.119	2,415
	expt				152.4	3.36	2,305
RgH	dz	152.7	1.491	2,759	151.9	2.578	2,805
	tz	152.1	1.586	2,766	150.9	2.830	2,839
	qz	152.0	1.610	2,771	150.8	2.926	2,836
	extrap	151.9	1.643	2,779	150.6	3.057	2,831

The results obtained here are consistent with previous work, cited above. MP2 somewhat underestimates the bond length and overestimates the dissociation energy and harmonic frequency, as is well known.

The second set of sample calculations has been performed on the coinage metal fluorides AuF and RgF, using the basis sets from this work for the metal and the aug-cc-pvnz basis sets of Dunning [16] for F. Results are reported in Table 12 for calculations without and with the dipole polarizing functions on the metal. The latter are indicated by +dp following the basis designation. As was found for the hydrides, addition of the diffuse functions has the largest effects for the dz basis sets and diminishes in importance as the basis set size increases.

RgF is considerably less bound than AuF, by about 0.7 eV, but the bond is shorter and the potential curve is

Table 11 Bond length, dissociation energy, and vibrational frequency of RgH as a function of basis set size and inclusion of diffuse functions

Basis	SCF			MP2		
	r_e/pm	D_e/eV	ω_e/cm^{-1}	r_e/pm	D_e/eV	ω_e/cm^{-1}
No diffuse						
dz	152.7	1.491	2,759	151.9	2.578	2,805
tz	152.1	1.586	2,766	150.9	2.830	2,839
qz	152.0	1.610	2,771	150.8	2.926	2,836
Diffuse on Rg only						
dz	152.8	1.496	2,736	151.9	2.660	2,791
tz	152.1	1.596	2,759	151.0	2.856	2,819
qz	152.0	1.612	2,762	150.8	2.937	2,827
Diffuse on H only						
dz	152.7	1.498	2,759	152.1	2.589	2,789
tz	152.0	1.588	2,758	151.0	2.840	2,831
qz	152.0	1.612	2,763	150.7	2.930	2,834
Diffuse on both						
dz	152.7	1.503	2,743	152.0	2.672	2,791
tz	152.1	1.597	2,760	151.0	2.859	2,823
qz	152.0	1.614	2,762	150.7	2.939	2,836

Table 12 Bond length, dissociation energy, and vibrational frequency of coinage metal hydrides as a function of basis set size

Molecule	Basis	SCF			MP2		
		r_e/pm	D_e/eV	ω_e/cm^{-1}	r_e/pm	D_e/eV	ω_e/cm^{-1}
AuF	dz	198.2	1.239	513	197.2	2.965	515
	tz	196.6	1.300	524	192.8	3.030	557
	qz	196.3	1.324	526	191.9	3.140	567
	extrap	195.9	1.357	530	190.7	3.295	582
	dz+dp	198.3	1.299	514	196.0	2.849	533
	tz+dp	196.5	1.324	523	192.5	3.027	559
	qz+dp	196.3	1.330	525	191.6	3.131	568
	extrap	196.1	1.339	527	190.5	3.275	581
RgF	dz	190.1	0.402	687	191.7	2.007	659
	tz	188.1	0.585	707	188.6	2.238	696
	qz	187.8	0.640	712	187.8	2.385	709
	extrap	187.4	0.717	717	186.8	2.590	724
	dz+dp	190.2	0.418	683	191.2	1.936	666
	tz+dp	188.0	0.601	709	188.4	2.244	699
	qz+dp	187.8	0.645	713	187.8	2.386	711
	extrap	187.5	0.706	718	186.9	2.582	726

steeper. The weakening of the bond is no doubt related to the higher ionization potential of Rg, and the difference in electron configuration. This is also consistent with the results of others [36, 37].

Table 13 Bond length r_e, atomization energy A_e, Mulliken charges, and metal *n*s population of Au and Rg halides at the DHF level of theory

Molecule	r_e/pm	A_e/eV	Metal charge	Metal *n*s
AuF	198.2	1.239	0.74	0.40
AuF_2^-	200.0	4.735	0.59	0.86
AuF_4^-	191.2	6.995	1.89	0.48
RgF	190.1	0.402	0.52	0.80
RgF_2^-	199.5	3.956	0.46	1.54
RgF_4^-	196.5	7.132	1.90	0.79
AuCl	232.2	1.778	0.50	0.48
$AuCl_2^-$	238.2	4.486	0.36	0.72
$AuCl_4^-$	232.9	5.845	0.61	0.71
RgCl	224.0	0.336	0.23	1.67
$RgCl_2^-$	234.1	3.091	0.26	1.27
$RgCl_4^-$	235.6	5.653	0.86	0.92

Finally, some calculations on metal mono, di, and tetrahalide species were done with the dz basis sets for the metals and the aug-cc-pvdz basis sets for the halogens. Calculations in larger basis sets were not possible due to limitations of the code, but these results serve as semi-quantitative illustrations of the use of the basis sets. The polyatomic fluorides have been studied previously by Seth et al. [41, 42].

Bond lengths, atomization energies, symmetric stretching harmonic frequencies, Mulliken charges and Mulliken populations of the *n*s spinor for group 11 fluorides and chlorides at the DHF level of theory are presented in Table 13. At the MP2 level of theory, bond lengths and atomization energies are presented in Table 14, along with the energies of the reactions $MX_2^- \rightarrow MX + X^-$ (in the row for MX_2^-) and $MX_4^- \rightarrow MX_2^- + F_2$ (in the row for MX_4^-).

From the atomization energies, the monovalent halides are less stable for Rg than for Au, but the trivalent halides are about as stable, at the DHF level. This means that the trivalent state is relatively more stable for Rg than for Au. The picture changes somewhat at the MP2 level, where both the monovalent and the trivalent halides are less stable for Rg than for Au; however, the trivalent state is more stable relative to the monovalent state for Rg than for Au, by about 0.4 eV. This is in agreement with the findings of Seth et al. [41]. Comparing the bond lengths, the dihalide anions of Rg and Au have similar bond lengths, but the tetrahalides of Rg have somewhat longer bonds. The monovalent Rg halides have smaller net charges than those of Au, but the trivalent halides have comparable or larger charges for Rg than for Au. The increased stability of the s spinors in Rg over Au is evident from the s populations.

Results for the group 12 mono, di, and tetrahalides are given in Table 15. The monohalides are fairly weakly bound for Hg at the DHF level and are unbound for Cn. Correlation stabilizes these species, but the Cn halides

Table 14 Bond length, atomization energy, and reaction energy ΔE_e for the reactions $MX_2^- \rightarrow MX + X^-$ and $MX_4^- \rightarrow MX_2^- + X_2$, for Au and Rg halides at the MP2 level of theory

Molecule	r_e/pm	A_e/eV	ΔE_e/eV
AuF	197.2	2.965	
AuF_2^-	200.6	6.665	3.700
AuF_4^-	195.0	10.073	2.045
RgF	191.7	2.007	
RgF_2^-	201.6	5.816	3.809
RgF_4^-	200.0	9.648	2.469
AuCl	227.2	2.541	
$AuCl_2^-$	233.3	5.657	3.116
$AuCl_4^-$	233.5	8.961	1.511
RgCl	222.2	1.314	
$RgCl_2^-$	233.4	2.781	1.467
$RgCl_4^-$	236.1	6.546	1.972

Table 15 Bond length, atomization energy, and reaction energy $MX_n \rightarrow MX_{n-2} + X_2$ of metal halides as a function of basis set size

Molecule	SCF		MP2		
	r_e/pm	A_e/eV	r_e/pm	A_e/eV	ΔE_e/eV
HgF	203.0	0.390	205.7	1.470	
HgF_2	192.9	2.782	195.4	5.493	4.130
HgF_4	185.9	0.231	194.3	7.044	0.188
HgCl	241.3	0.647	242.1	0.773	
$HgCl_2$	231.0	3.185	230.3	4.006	2.213
$HgCl_4$	232.9	0.735	236.4	4.362	−1.437
CnF	199.2	−0.596	207.0	0.581	
CnF_2	191.5	1.300	195.2	3.978	2.614
CnF_4	190.7	0.514	196.1	6.344	1.003
CnCl	241.0	−0.408	254.9	0.214	
$CnCl_2$	228.6	1.642	230.0	2.640	0.847
$CnCl_4$	232.9	0.742	236.0	3.704	−0.729

remain less stable than the Hg halides. This is in line with the higher ionization potential for Cn. The tetrafluorides are more stable than the difluorides: marginally so for Hg, but more so for Cn, in line with the results of Seth et al. [42]. However, the tetrachlorides are less stable than the dichlorides, although less so for Cn than for Hg, so the IV oxidation state is only likely to be stable in CnF_4.

One note of warning needs to be sounded here, however. The present results are only of dz quality, and the energy values in a larger basis set and with more correlation could present a different picture. As an example, the $CnF_2 \rightarrow Cn + F_2$ reaction is lowered by about 0.6 eV on going to a tz basis set, due partly to the better description of the F_2 bond energy.

The conclusion of these polyatomic studies is that the higher oxidation state is relatively more stable than the lower oxidation state for Cn and Rg compared to Hg and Au, in agreement with the findings of Seth et al. [41, 42]. Overall, though, the Rg and Cn compounds are less thermodynamically stable than the corresponding Hg and Au compounds, based on the atomization energies—at least in the gas phase. Thus, these 6d elements are more "noble" than their 5d counterparts. For Rg, the balance might change if the cohesive energy of Rg is sufficiently smaller than that of Au. The calculations of Liu and van Wüllen [36] on the dimers of Au and Rg indicate that Rg_2 is indeed less strongly bound than Au_2, which would support a lower cohesive energy for Rg. Hg and Cn, on the other hand, are fairly weakly bound anyway, so the cohesive energy is not likely to make much difference.

6 Internet archives

The full tables of basis sets including spin-free relativistic SCF [43] and Dirac-Fock SCF coefficients are available in ASCII format as an Internet archive and also from the Dirac Web site, http://dirac.chem.sdu.dk. 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 for the construction of various basis sets.

The output files from the MR-CISD calculations for all elements, basis sets, and ionization states are available as an Internet archive. These files list the configurations, the absolute and relative energies of the states, and contributions from the most important configurations.

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