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LETTER

Revised relativistic basis sets for the 5*d* elements Hf–Hg

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Abstract The relativistic double-zeta (dz) and triple-zeta (tz) basis sets for the 5*d* elements Hf–Hg have been revised for consistency with the recently optimized 4*f* basis sets. The new dz basis sets have 24 *s* functions instead of 22 *s* functions, and the new tz basis sets have 30 *s* functions instead of 29 *s* functions. New contraction patterns have been determined, including the 6*p* orbital.

Keywords Gaussian basis sets · Relativistic basis sets · 5*d* elements · Double zeta · Triple zeta · Correlating functions

This communication describes revisions to the previously published basis sets for the 5*d* transition elements, Hf–Hg [1]. In the course of developing basis sets for the lanthanides and the *s* block, the *s* sets for the 5*d* block were noted to be smaller than was consistent with the 4*f* set [2], 6*s* set [3], and 6*p* set [4, 5]. To ensure consistency of the entire series of basis sets, a set of 24 *s* functions has been optimized for the double-zeta (dz) basis sets, and a set of 30 *s* functions has been optimized for the triple-zeta (tz) basis sets. The *s* functions were optimized on the 1:1 weighted average of the $d^n s^2$ and $d^{n+1} s^1$ configurations, with the remaining angular spaces kept the same size and kept fixed, using the same optimization methods as the original set [1].

The original optimization was done on the $d^n s^2$ configuration, which gives a somewhat more compact *d* set. The change to the weighted average of the two configurations was made because both configurations are important and have low-lying states. It has also been found that the relative energies of the states of the $d^n s^2$ and $d^{n+1} s^1$ configurations for Ag were best reproduced with a weighted average of the contracted functions, and therefore a balance between the two configurations is needed [6]. Mixing of these two configurations is important for bonding, such as for formation of *sd* hybrids. For these reasons, the *d* set was also reoptimized with the 1:1 weighted average of the $d^n s^2$ and $d^{n+1} s^1$ configurations, for both the dz and the tz basis sets, with the remaining angular spaces kept fixed.

To complete the reoptimization, the *p* and *f* sets were also reoptimized. For the *f* set, the correlating functions that had been added to the original basis were kept fixed, and the rest reoptimized. In the *p* space, the dz 17*p* set and the tz 21*p* set, which do not include the 6*p* orbital, were reoptimized first, and then the functions for the 6*p* were added, and the functions for the antinodes of the 3*p* through 6*p* orbitals were reoptimized, fixing the functions for the 2*p*. This procedure is the same as used for the optimization of the 4*f* basis sets.

For the quadruple-zeta basis sets, a test reoptimization of one of the *s* sets on the same weighted average produced no significant change in the exponents, so it was not considered necessary to reoptimize the quadruple-zeta basis

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sets. These sets are large enough that the changes due to the configuration are not significant.

In the original paper [1], problems of collapse were found in determining the contraction pattern for the 5*s* and 5*p* shells, which were traced to inappropriate large-small component ratios as determined by the free-particle model used. Subsequently, an alternative method was developed that is not subject to these issues [6]. This method has been used to redetermine the primitive functions that should be added to the SCF functions to form a flexible contracted basis. The 6*p* has also been included in the set of contracted functions. The SCF calculations for the contraction coefficients were performed on the weighted average of the d^ns^2, $d^{n+1}s^1$, and d^np^2 configurations with weights of 45, 45, and 10%, except for Hg where the d^ns^2 and d^np^2 configurations were used with weights of 90 and 10%. The total DHF energies for the weighted average used in the contracted basis sets are given in Table 1. These are provided as a reference for generating the contraction. The total DHF energies of the configuration average of the $5d^n6s^2$ configuration and of the $5d^{n+1}6s^1$ configuration in the uncontracted basis sets are given in Table 2 as a reference for calculations, along with the numerical energy calculated with GRASP [7].

Table 1 Configuration average total DHF energies in E_h for uncontracted basis set calculations on the weighted average of configurations used for the contraction

Element	Double-zeta	Triple-zeta
Hf	−15,088.688003	−15,088.718719
Ta	−15,616.536078	−15,616.567206
W	−16,156.095423	−16,156.127312
Re	−16,707.535515	−16,707.568415
Os	−17,271.003792	−17,271.037873
Ir	−17,846.716501	−17,846.751956
Pt	−18,434.809044	−18,434.846005
Au	−19,035.468526	−19,035.507128
Hg	−19,648.814677	−19,648.853908

Table 2 Configuration average total DHF energies in E_h for uncontracted basis set and numerical calculations on the configuration average of the $5d^n6s^2$ and the $5d^{n+1}6s^1$ configurations

Element	Double-zeta	Triple-zeta	Numerical
$5d^n6s^2$			
Hf	−15,088.754425	−15,088.784414	−15,088.786607
Ta	−15,616.598185	−15,616.628646	−15,616.630785
W	−16,156.152060	−16,156.183293	−16,156.185412
Re	−16,707.585779	−16,707.618016	−16,707.620132
Os	−17,271.046929	−17,271.080332	−17,271.082449
Ir	−17,846.751860	−17,846.786619	−17,846.788751
Pt	−18,434.836045	−18,434.872288	−18,434.874439
Au	−19,035.486647	−19,035.524508	−19,035.526683
Hg	−19,648.854743	−19,648.893987	−19,648.896156
$5d^{n+1}6s^1$			
Hf	−15,088.668742	−15,088.700821	−15,088.703235
Ta	−15,616.529544	−15,616.561990	−15,616.564336
W	−16,156.102384	−16,156.135589	−16,156.137906
Re	−16,707.556679	−16,707.590911	−16,707.593216
Os	−17,271.039817	−17,271.075253	−17,271.077553
Ir	−17,846.768004	−17,846.804840	−17,846.807153
Pt	−18,434.876608	−18,434.914977	−18,434.917309
Au	−19,035.552706	−19,035.592744	−19,035.595100

Flexible contracted basis sets can be constructed by using the SCF occupied functions (including the 6*p*) as the contracted functions, and adding primitive functions, in the same way as in the correlation-consistent basis sets [8]. The list of primitives to be added for each occupied angular momentum and each basis set for the correlation of the various shells is given in Table 3. In addition, functions of higher angular momentum (*g* and higher) should be added from the correlating sets described in the original paper [1]. In this table, the functions are counted from the function with the smallest exponent to the function with the largest exponent. For example, to construct a tz basis set that includes functions for correlation of the 5*d* and 6*s* shells, the table indicates that you should add *s* functions 3 and 1, *p* functions 3 and 1, the first three *d* functions and the first two *f* functions to the SCF occupied functions. The sets reported in this table overlap; in a calculation that includes overlapping sets, duplicates should be discarded.

Table 3 Indices of primitive functions to be used in a basis set composed of the SCF functions plus primitives

Shells	Angular space	Double-zeta	Triple-zeta	Quadruple-zeta
5*d*, 6*s*	*s*	2	3, 1	4, 2, 1
	p	1	3, 1	3, 2, 1
	d	2, 1	3, 2, 1	4, 3, 2, 1
	f	1	2, 1	3, 2, 1
5*s*, 5*p*	*s*	4	6, 4	8, 6, 5
	p	3	6, 4	8, 6, 5
	d	3	4, 3	6, 5, 4
	f		3	4, 3
4*f*	*s*	5	9, 7	11, 10, 9
	p	5	8, 7	12, 11, 10
	d	4	5, 4	9, 8, 7
	f	2	4, 3	7, 5, 4

The list of indices of the primitives is given for the correlation of each of three sets of shells for each basis set size. The exponents are counted from the smallest, starting at 1

To test the changes in the basis sets, two sets of calculations were performed. In the first, the transition energies

Table 4 Valence DHF transition energies in eV of Au as a function of basis set reoptimization

Basis	Optimization	$E_{5/2} - E_{1/2}$	$E_{3/2} - E_{1/2}$	$E_{3/2} - E_{5/2}$
dz	Old	1.17437	2.64510	1.47073
	New *s*	1.18775	2.65827	1.47052
	New *sd*	1.20975	2.68037	1.47062
	New all	1.20927	2.67997	1.47070
tz	Old	1.26376	2.73397	1.47022
	New *s*	1.26379	2.73400	1.47022
	New *sd*	1.26878	2.73902	1.47024
	New all	1.26869	2.73894	1.47025
Numerical		1.27360	2.74389	1.47029

The transitions are between the $5d^{10}6s^1$ J = 1/2 ground state and the spin-orbit components of the $5d^96s^2$ state, which have J = 3/2 and J = 5/2, and between the spin-orbit components

were calculated between the three valence states of Au, $5d^{10}6s^1$ J = 1/2, $5d^96s^2$ J = 5/2, and $5d^96s^2$ J = 3/2. Separate DHF calculations were performed on the $5d^96s^2$ spin-orbit doublet and the $5d^{10}6s^1$ state in the uncontracted basis sets. Calculations were done for the basis sets at various stages of the reoptimization, to assess the effects of each stage: optimization of the new *s* sets, reoptimization of the *d* sets, and reoptimization of the *p* and *f* sets. The results are given in Table 4, along with the numerical results. The differences are given to five decimals so that the small size of the changes can be noted. The spin-orbit splitting varies by about 0.2 meV for the dz basis and 0.02 meV for the tz basis sets, which are very small changes. The changes in the excitation energies between the configurations are a little larger—35 meV for the dz basis and 5 meV for the tz basis. The reoptimization of the *s* gives less than half the total change in the excitation energies. The dz change is almost at the 4 kJ/mol level of “chemical accuracy”, so the reoptimization of both *d* and *s* sets is not entirely insignificant. Reoptimization of the *p* and *f* sets affected the energies by less than 1 meV.

The second set of calculations was done on the AuH molecule, using the old basis set and the fully optimized new basis set. The contraction pattern used was the same for both optimizations, and included only the valence 5*d* and 6*s* flexibility. DHF and MP2 calculations were performed at seven points around the minimum spaced at 5 pm, and the counterpoise-corrected curve was fitted to a quartic polynomial. Extrapolation was performed on the tz and qz results using a $1/n^3$ function [9]. The results are reported in Table 5. The differences are small for the most part, especially the DHF results. The largest change is a 7-meV increase in the tz MP2 dissociation energy and a concomitant 11-meV reduction in the extrapolated MP2 dissociation energy. The 10 cm^{-1} change in the vibrational frequency at the MP2 level is probably not significant, as the sensitivity of the frequencies to the set of seven points selected for the fit is about 5 cm^{-1}.

Table 5 Bond length, dissociation energy and vibrational frequency of AuH for old and new basis sets as a function of basis set size

Optimization	Basis	SCF			MP2		
		r_e/pm	D_e/eV	$\omega_e/\mathrm{cm}^{-1}$	r_e/pm	D_e/eV	$\omega_e/\mathrm{cm}^{-1}$
Old basis	dz	156.9	1.751	2099	152.0	2.739	2335
	tz	156.7	1.793	2097	150.7	2.952	2392
	qz	156.7	1.807	2101	150.4	3.027	2406
	Extrap	156.6	1.826	2111	150.1	3.130	2425
New basis	dz	157.0	1.749	2099	152.0	2.740	2327
	tz	156.7	1.793	2098	150.7	2.959	2399
	qz	156.7	1.807	2103	150.4	3.027	2406
	Extrap	156.6	1.826	2109	150.1	3.119	2415
Experiment [10]					152.4	3.36	2305

Table 6 Bond length, dissociation energy and vibrational frequency of AuH as a function of inclusion of diffuse functions and basis set size

Basis	Diffuse functions	SCF			MP2		
		r_e/pm	D_e/eV	$\omega_e/\mathrm{cm}^{-1}$	r_e/pm	D_e/eV	$\omega_e/\mathrm{cm}^{-1}$
dz	None	157.0	1.749	2099	152.0	2.740	2327
	H	157.0	1.746	2102	152.1	2.785	2331
	Au	157.1	1.779	2087	151.8	2.785	2349
	Both	157.1	1.779	2089	151.9	2.829	2347
tz	None	156.7	1.793	2098	150.7	2.959	2399
	H	156.7	1.793	2097	150.6	2.979	2391
	Au	156.7	1.808	2104	150.8	2.986	2405
	Both	156.7	1.809	2103	150.8	2.996	2398
qz	None	156.7	1.807	2103	150.4	3.027	2406
	H	156.7	1.808	2104	150.3	3.046	2412
	Au	156.7	1.811	2104	150.4	3.043	2422
	Both	156.7	1.811	2104	150.3	3.053	2418
Extrap	None	156.6	1.826	2109	150.1	3.119	2415
	H	156.6	1.829	2113	149.9	3.137	2439
	Au	156.7	1.815	2105	149.9	3.122	2445
	Both	156.6	1.815	2106	149.7	3.131	2444

In addition to these calculations, a set of calculations was done on the AuH molecule to test the effect of the addition of diffuse functions on the bond length, dissociation energy, and harmonic frequency. The results are reported in Table 6. At the SCF level, only the dipole polarizing functions on the Au make a difference, but at the correlated level, the diffuse functions on H also make a difference to the properties. It is therefore recommended that the dipole polarizing functions are included in the basis for higher accuracy.

The full tables of basis sets, including exponents, contraction coefficients, correlating and dipole polarizing functions, are available in ASCII format from the Dirac web site at http://dirac.chem.sdu.dk/basisarchives/dyall, and in an Internet archive with this paper. The contraction coefficients include the Dirac-Fock SCF coefficients, and the spin-free relativistic SCF [11] coefficients along with the Foldy-Wouthuysen transformed large component coefficients that can be used in the scalar one-electron NESC approximation [12]. Prescriptions are given for the construction of various basis sets.

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