Theor Chem Acc (2004) 112: 403–409
DOI 10.1007/s00214-004-0607-y

Theoretical
Chemistry Accounts

Regular article

Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 5*d* elements Hf–Hg

Kenneth G. Dyall

Schrödinger, Inc., 1500 SW First Ave Suite 1180, Portland, OR 97201, USA

Received: 7 December 2003 / Accepted: 26 July 2004 / Published online: 16 November 2004

Abstract. Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized for the 5*d* elements Hf–Hg. The basis sets include self-consistent-field exponents for the occupied spinors and for the 6*p* shell, exponents of correlating functions for the valence shell and the 4*f* shell, and exponents of functions for dipole polarization of the valence 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.

Key words: Gaussian basis sets – Relativistic basis sets – 5*d* elements – Double zeta – Triple zeta – Quadruple zeta

1 Introduction

Relativistic effects have long been known to be important for heavy elements [1]. However, in order to perform calculations on molecules containing heavy elements with existing codes and algorithms, Gaussian basis sets are needed.

By far the majority of calculations on heavy elements have been performed with relativistic effective core potentials (ECPs) [2]. Many of the commonly used ECP sets [3,4,5] are provided with basis sets of only double-zeta (dz) or triple-zeta (tz) quality, though the basis sets provided by the Stuttgart group [6] for their pseudopotentials tend to be larger. Christiansen [7] has offered a prescription for the selection of correlating functions for ECPs . Recently, this lack has been filled by a number of new basis sets. For the 4*p*, 5*p*, and 6*p* elements, atomic natural orbital (ANO) basis sets have been optimized by Osanai et al. [8], correlation-consistent[9] basis sets of dz to quintuple-zeta quality have been optimized by Peterson and workers [10,11] for the small-core Stuttgart pseudopotentials [6], and for the 4*p* and 5*p* elements, correlation-consistent basis sets of tz- and quadruple-zeta (qz) quality have been optimized by Martin and Sundermann [12] for the large-core Stuttgart pseudopotentials. ANO basis sets of dz and tz quality have very recently been optimized by Osanai et al. [13] for the 5*d* elements, the subject of this paper.

In the 1980s, the Douglas–Kroll–Hess method [14,15] emerged as the first viable all-electron method for variational inclusion of scalar relativistic effects. The method was originally developed to second order, but has recently been extended to third [16] and higher order [17]. Basis sets of approximately tz quality have been optimized with the third-order Douglas–Kroll method [18], but these basis sets do not include correlating or polarizing functions.

Four-component relativistic methods have also been under active development in the last 20 years, resulting in a combined effort with the codes MOLFDIR [19] and Dirac [20], which provide self-consistent-field (SCF) and correlated methods, in addition to properties. Basis sets for four-component methods have also been under active development by the author and collaborators. Fægri [21] has published SCF basis sets of dz quality or better for the entire periodic table. The author has published dz and tz basis sets for the 4*p*, 5*p*, and 6*p* elements [22,23], including core and valence correlating functions and diffuse functions, in the style of the correlation-consistent basis sets.

This paper reports relativistic dz, tz, and qz basis sets for the 5*d* elements Hf–Hg. In addition to the SCF sets, which include functions to describe the 6*p* shell, the basis sets include high angular momentum correlating functions for the 5*d* shell, the 5*s* and 5*p* shells, and the 4*f* shell, and functions for dipole polarization of the 5*d* shell. Prescriptions for the selection of primitive functions for basis set flexibility and electron correlation are provided.

2 Methods

The methods used have been described previously [22,23,24]. As for the previous basis sets, ℓ-optimization was employed. The SCF basis sets were optimized on the

---

Correspondence to: K. G. Dyall
e-mail: dyall@schrodinger.com

average energy of the nonrelativistic $d^n s^2$ configuration, both in the SCF calculations and the multireference singles and doubles configuration interaction (MR-SDCI) calculations.

SCF optimizations were performed on the Hg atom to determine the size of each angular space for each basis set, dz, tz, and qz. A reference basis set was chosen and sets of different size were optimized for each angular space to determine the optimal set. This optimum was determined by considering the distribution of exponents among the maxima of all the orbitals, the energy balance between the angular spaces, and the match with the already published basis sets for the 6*p* main group elements.

The definition of dz, tz and qz for the basis sets presented here needs some explanation. For the main group elements, 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. To maintain good energy balance, the number of exponents in the outermost maximum of the outer core *d* shell is one higher: thus the dz basis sets for the main group elements have three functions representing the outermost maximum of the sub-valence *d* shell. This relation is carried over into the basis set definitions for the 5*d* block. The dz basis set has three exponents for the 5*d* outermost maximum, the tz basis set has four, and the qz basis set has five.

Exponents were optimized for the 6*p* orbital in separate calculations on the $5d^n 6p^2$ configuration. Two, three and four exponents were added for the dz, tz and qz basis sets. For the dz and tz, basis sets, the outermost four and six exponents were optimized, respectively, covering the outermost maxima of the 5*p* and 6*p* orbitals. The reason for reoptimizing more than just the added functions is that the spacing of the exponents for the 5*p* 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 5*p* orbital no longer need to describe the tail, and can be reoptimized. For the qz basis set, the density of functions is higher, and some adjustment further in than the 5*p* orbital was considered necessary, so half the exponents in the set were reoptimized to obtain a better distribution. This procedure was found to give a better description of the SCF occupied orbitals in the ground state as well.

Valence correlating functions were optimized in MR-SDCI calculations on the $d^n s^2$ configuration, using the RAMCI program [25] modified for basis set optimization. All states of this configuration, weighted by their *J* value, were included in the optimization. For the dz and tz basis sets, all single and double excitations out of the 5*d* and 6*s* orbitals were included in the CI expansion. Single and double excitations out of the 5*d* shell only were considered for the qz basis set, to limit the size of the CI calculations. The correlating function spaces were 1*f* for the dz basis set, 2*f*1*g* for the tz basis set, and 3*f*2*g*1*h* for the qz basis set.

The overlap of the correlating *f* functions with the SCF functions that describe the 4*f* orbital was handled as follows. For the dz basis set, the correlating *f* function was added to the basis set, and the SCF *f* functions were reoptimized. For the tz basis set, the largest correlating exponent was larger than the smallest SCF exponent. This SCF exponent was replaced by the two correlating exponents, which resulted in a higher SCF energy, by several millihartrees. The remaining SCF exponents were then reoptimized, resulting in a lower SCF energy than the original set. For the qz basis set, the three correlating exponents were similar to the outer three SCF exponents, but a bit smaller. The outer three SCF exponents were replaced by the correlating exponents, and the remaining SCF exponents reoptimized to regain most of the lost energy resulting from the replacement.

Correlating functions for the 4*f* core shell were also optimized in MR-SDCI calculations. Only those double excitations out of the 4*f* shell that coupled to $J = 0$ were included in the CI expansion. The correlating function spaces were 1*g* for the dz basis set, 2*g*1*h* for the tz basis set, and 3*g*2*h*1*i* for the qz basis set.

Functions for dipole polarization of the valence 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 $d \rightarrow f$ excitation. For the tz basis sets, the most diffuse correlating function is larger than the polarizing *f* function for the dz basis set. The correlating *f* set was therefore extended in an even-tempered sequence to produce a diffuse *f* function. A diffuse *g* function was determined by applying the same ratio used to extend the *f* set to the correlating *g* function. Similarly, for the qz basis sets, the *f* and *g* sets were extended in an even-tempered sequence, and the ratio used for the *g* set was applied to the *h* function to obtain a diffuse *h* function.

Table 1 Configuration average total self-consistent field (*SCF*) energies in hartrees for uncontracted basis set and numerical calculations on the $d^n s^2$ configuration

Element	Double-zeta	Triple-zeta	Quadruple-zeta	Numerical
Hf	−15088.75090293	−15088.78438053	−15088.78632294	−15088.78660723
Ta	−15616.59449126	−15616.62859031	−15616.63061342	−15616.63078504
W	−16156.14828357	−16156.18322588	−16156.18532864	−16156.18541220
Re	−16707.58194082	−16707.61794224	−16707.62012066	−16707.62013174
Os	−17271.04304778	−17271.08025200	−17271.08250248	−17271.08244860
Ir	−17846.74790481	−17846.78653312	−17846.78886276	−17846.78875058
Pt	−18434.83201767	−18434.87219746	−18434.87460640	−18434.87443919
Au	−19035.47050330	−19035.52441252	−19035.52690448	−19035.52668278
Hg	−19648.85022305	−19648.89385550	−19648.89643688	−19648.89615637

The contraction coefficients for the SCF occupied orbitals were obtained from calculations on the average of the d^ns^2 and $d^{n+1}s^1$ configurations. The individual configuration state functions (CSFs) in each configuration were weighted by their degeneracy $(2J + 1)$, and the weights were scaled so that the weight of each configuration was equal.

To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed on Hf and Hg, 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 $5s5p$ correlation in the tz basis sets, the correlating set was $2s2p2d1f$. Excitations into the $5d$ shell were not considered in these calculations. The ratio of the large component to the small component for each primitive function was taken to be the free-particle ratio. The primitive spinors so determined were Schmidt-orthogonalized to the SCF occupied spinors and to each other.

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 Hg and for Hf, a compromise that gave the smallest error for either element was chosen. This procedure was used for $5d6s$ correlation, $5s5p$ correlation, and $4f$ correlation. In some cases, exponents were optimized for Hf and Hg, and compared with SCF exponents. For $5s5p$ correlation in the qz basis sets, an extra g function was required, because the exponent of the optimal g function was between those of the valence correlating set and the $4f$ correlating set. The exponent of this function was taken to be the geometric mean of the smallest exponent of the $4f$ correlating set and the largest exponent of the valence correlating set.

3 Primitive basis sets

The SCF basis set sizes were determined to be $22s17p12d7f$ for the dz set, $29s21p15d9f$ for the tz set, and $34s26p19d12f$ for the qz set. With the p functions for the $6p$ orbitals and the correlating function substitutions in the f space, the final SCF basis set sizes were $22s19p12d8f$ for the dz set, $29s24p15d10f$ for the tz set, and $34s30p19d12f$ for the qz set.

Configuration average total energies for the d^ns^2 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

Table 2 Configuration average total SCF energies in hartrees for uncontracted basis set calculations on the d^ns^2 and $d^{n+1}s^1$ configurations

Element	Double-zeta	Triple-zeta	Quadruple-zeta
Hf	−15088.70411652	−15088.73951401	−15088.74174148
Ta	−15616.55560925	−15616.59124343	−15616.59347761
W	−16156.11813380	−16156.15449203	−16156.15676974
Re	−16707.56132953	−16707.59870249	−16707.60103664
Os	−17271.03269868	−17271.07126136	−17271.07365508
Ir	−17846.74847047	−17846.78846045	−17846.79092549
Pt	−18434.84409714	−18434.88565056	−18434.88818973
Au	−19035.50668978	−19035.54995160	−19035.55256991
Hg	−19648.85022305	−19648.89385550	−19648.88773477

Table 3 Exponents of valence correlating and polarizing f functions and $4f$ correlating g function for the double-zeta basis sets

Element	Correlating f	Polarizing f	Correlating g
Hf	0.38547549	0.11195327	7.1448282
Ta	0.47476634	0.14059344	7.7301267
W	0.56143065	0.15925621	8.3273766
Re	0.64713929	0.19237380	8.9360799
Os	0.73285164	0.21776801	9.5561343
Ir	0.81914535	0.24625192	10.187605
Pt	0.90639763	0.26863666	10.830621
Au	0.99485802	0.30537602	11.485338
Hg	1.0847115	0.34059395	12.151916

Table 4 Exponents of valence correlating $2f1g$ functions for the triple-zeta basis sets

Element	f	f	g
Hf	0.57254774	0.17022026	0.29847606
Ta	0.73694308	0.22091547	0.41192863
W	0.88976809	0.27458712	0.54155215
Re	1.0367851	0.32833657	0.67336535
Os	1.1791247	0.38129037	0.80311377
Ir	1.3182035	0.43354460	0.93231313
Pt	1.4557480	0.48555165	1.0637733
Au	1.5926764	0.53758925	1.2007077
Hg	1.77363780	0.61209188	1.3625828

Table 5 Exponents of valence polarizing $1f1g$ functions for the triple-zeta basis sets

Element	f	g
Hf	0.05060702	0.08873788
Ta	0.06622444	0.12348499
W	0.08473903	0.16712585
Re	0.10397999	0.21324619
Os	0.12329684	0.25970073
Ir	0.14258870	0.30662893
Pt	0.16195139	0.35481201
Au	0.18145695	0.40528481
Hg	0.21123618	0.47023460

Table 6 Exponents of $2g1h$ functions for $4f$ correlation for the triple-zeta basis sets

Element	g	g	h
Hf	13.085729	3.9047003	8.3954836
Ta	14.159365	4.2905061	9.0842505
W	15.246189	4.6826567	9.7873952
Re	16.347183	5.0813075	10.504277
Os	17.463582	5.4868196	11.234718
Ir	18.596282	5.8993841	11.978760
Pt	19.746166	6.3192532	12.736535
Au	20.914003	6.7466704	13.508228
Hg	22.100378	7.1817732	14.294006

Table 7 Exponents of valence correlating $3f2g1h$ functions for the quadruple-zeta basis sets

Element	f	f	f	g	g	h
Hf	1.0876844	0.40757909	0.14970359	0.82870055	0.26099265	0.62848241
Ta	1.2637906	0.49140560	0.18408649	0.98076324	0.32068644	0.74058021
W	1.4303266	0.57199483	0.21756792	1.1247807	0.37896220	0.84961092
Re	1.5912492	0.65110611	0.25079181	1.2659138	0.43783171	0.95789072
Os	1.7495829	0.72991987	0.28417474	1.4067982	0.49855647	1.0667409
Ir	1.9067697	0.80900327	0.31790680	1.5483638	0.56189520	1.1763233
Pt	2.0640420	0.88882536	0.35215489	1.6921677	0.62926925	1.2875573
Au	2.2220809	0.96965516	0.38700265	1.8387652	0.70210737	1.4004498
Hg	2.3819196	1.0518378	0.42255517	1.9905625	0.78325320	1.5156635

Table 8 Exponents of valence polarizing $1f1g1h$ functions for the quadruple-zeta basis sets

Element	f	g	h
Hf	0.05498605	0.08219756	0.19793554
Ta	0.06896103	0.10485690	0.24215226
W	0.08275564	0.12768031	0.28625173
Re	0.09659951	0.15142943	0.33129818
Os	0.11063582	0.17668387	0.37804326
Ir	0.12492500	0.20390958	0.42688315
Pt	0.13952467	0.23400741	0.47880610
Au	0.15445806	0.26809011	0.53474262
Hg	0.16975324	0.30819709	0.59638835

Table 9 Exponents of $1g$ functions for $5s5p$ correlation for the quadruple-zeta basis sets

Element	g exponent
Hf	1.4437094
Ta	1.6597629
W	1.8690385
Re	2.0766690
Os	2.2852082
Ir	2.4956504
Pt	2.7094025
Au	2.9270188
Hg	3.1504569

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 problem probably only matters for properties that are sensitive to the details of the wave function near the nucleus [26], and in that case it would be preferable to replace the core part of the basis set with an even-tempered sequence of exponents. It should also be noted that obtaining the exact energy is a necessary but not sufficient condition for basis set convergence. It is always possible in a four-component relativistic calculation to obtain the exact energy with a wave function that is not exact.

Configuration average total Dirac–Hartree–Fock (DHF) energies from calculations using the uncontracted SCF basis sets for the average of the d^ns^2 and $d^{n+1}s^1$ configurations, equally weighted, 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.

The valence correlating functions, valence polarizing functions, and $4f$ core correlating functions for the dz basis sets are presented in Table 3. The valence correlating functions, valence polarizing functions, and $4f$ core correlating functions for the tz basis sets are presented in Tables 4, 5, and 6. The valence correlating functions, valence polarizing functions, g function for $5s5p$ correlation, and $4f$ core correlating functions for the qz basis sets are presented in Tables 7, 8, 9, and 10.

4 Contraction patterns

The MR-SDCI calculations that were performed to determine which functions to uncontract yielded the contraction patterns described this section. The contracted basis sets are formed by adding primitive functions to the SCF occupied spinor or orbital set. Three primary contraction patterns are described, for a valence basis set, which correlates the $5d$ and $6s$ orbitals; a valence plus outer core set which adds functions for $5s$ and $5p$ correlation to the valence set, and a valence plus outer core plus $4f$ set, which adds functions for $4f$ (and other $n = 4$ subshells) to the valence plus outer core set. To any of these contractions, the relevant polarization functions listed in Tables 3, 5, and 8 can be added.

Table 10 Exponents of $3g2h1i$ functions for $4f$ correlation for the quadruple-zeta basis sets

Element	g	g	g	h	h	i
Hf	20.326934	7.2241572	2.5151387	14.305240	4.8113483	9.3531825
Ta	22.023548	7.9160691	2.8088460	15.476073	5.2835023	10.140874
W	23.729636	8.6130364	3.1057652	16.663028	5.7638600	10.942537
Re	25.450142	9.3169818	3.4066727	17.866799	6.2525369	11.758159
Os	27.188428	10.029244	3.7121005	19.088506	6.7498413	12.588012
Ir	28.947485	10.750981	4.0224855	20.328954	7.2560214	13.432450
Pt	30.729387	11.483021	4.3381409	21.589026	7.7713582	14.291836
Au	32.536284	12.226182	4.6593438	22.869254	8.2960313	15.166536
Hg	34.368292	12.980604	4.9862182	24.170855	8.8304238	16.056775

The contraction patterns include an extra p function in the valence space, because the $6p$ orbital is counted as part of the valence space, even though it is not formally occupied.

In the descriptions, functions are counted by increasing exponent size, from the smallest. A designation of the basis set in terms of the contraction pattern is given at the end of each description in parentheses. In cases where linear dependence might be a problem, alternative prescriptions are given.

4.1 *Double-zeta basis sets*

- **Valence:** To the SCF functions, add the second s primitive, the first and second primitives from the p and d sets, and the valence correlating f function. (Hartree–Fock, HF plus $1s2p2d1f$ valence)
- **Valence plus outer core:** To the valence set, add the fourth s primitive, the third p primitive and the third d primitive. (HF plus $1s2p2d1f$ valence plus $1s1p1d$ outer core)
  If linear dependence problems are encountered in the d space, delete the $5d$ orbital, or do not add the third d primitive (on the grounds that the $5d$ orbital will be used to correlate the $5s$ and $5p$). As an option, delete the $6s$ orbital and add the first s primitive.
- **Valence plus outer core plus 4*f*:** To the valence plus outer core set, add the second and third f primitives, the fourth d primitive, and the core correlating g function. This choice reflects only $4f$ correlation with a change in angular momentum of 1 unit. If it is necessary to uncontract an s and p primitive, add the fifth s and p primitives to the set. (HF plus $1s2p2d1f$ valence plus $1s1p1d$ outer core plus $1d2f1g$ core)

4.2 *Triple-zeta basis sets*

- **Valence:** To the SCF functions, add the first and third s primitives, the first to third primitives from the p and d sets, the first and second f primitives, and the valence correlating g function. (HF plus $2s3p3d2f1g$ valence)
- **Valence plus outer core:** To the valence set, add the fourth and sixth s and p primitives, the fourth d primitive and the third f primitive. (HF plus $2s3p3d2f1g$ valence plus $2s2p2d1f$ outer core; d sets overlap)
  If linear dependence problems are encountered in the d space, use one of the following solutions:
  - Delete the $5d$ orbital, and optionally also delete the $6s$ orbital and add the second s primitive.
  - Do not add the fourth d primitive (on the grounds that the $5d$ orbital will be used to correlate the $5s$ and $5p$).
  - Add the fifth d primitive instead of the fourth (which results in a loss of about 11–16 mE_h in the $5s5p$ correlation energy)
- **Valence plus outer core plus 4f:** To the valence plus outer core set, add the fourth f primitive, the fifth d primitive, the seventh and eighth p and s primitives, and the core correlating $2g1h$ set. (HF plus $2s3p3d2f1g$ valence plus $2s2p2d1f$ outer core plus $2s2p2d2f2g1h$ core; d and f sets overlap)
  If linear dependence problems are encountered in the d space, omit the fourth d primitive or add the sixth and seventh d primitives instead of the fifth.

4.3 *Quadruple-zeta basis sets*

- **Valence:** To the SCF functions, add the first, second, and fourth s primitives, the first to fourth p and d primitives, the first to third f primitives, and the valence correlating $2g1h$ set. (HF plus $3s4p4d3f2g1h$ valence)
- **Valence plus outer core:** To the valence set add the fifth, sixth, and eighth s primitives, the sixth, seventh and eighth p primitives, the fifth and sixth d primitives, the fourth f primitive, and the outer core correlating g primitive. (HF plus $3s4p4d3f2g1h$ valence plus $3s3p3d2f1g$ outer core; d and f sets overlap.)
  If linear dependence problems are encountered in the d space, use one of the following solutions:
  - Delete the $5d$ orbital, and optionally also delete the $6s$ orbital and add the third s primitive

Table 11 Energy levels in reciprocal centimeters for the Pt atom from valence multi-reference singles and doubles configuration interation(*MR-SDCI*) calculations, for the double-zeta, triple-zeta, and quadruple-zeta basis sets. Experimental data from Ref. [27]. Valence CI includes only the three valence configurations; SDCI includes singles and doubles from these three configurations

J	Valence CI			SDCI			Expt
	Double-zeta	Triple-zeta	quadruple-zeta	Double-zeta	Triple-zeta	quadruple-zeta	
3	0	0	0	0	0	0	0
2	830	1048	1070	766	1147	1271	776
4	−854	−121	−45	375	2277	2726	824
0	17197	17480	17499	10207	8772	8456	6140
2	6129	6416	6446	6690	7408	7641	6567
3	8383	9135	9217	9316	11283	11547	10117
1	9177	9143	9138	9677	9690	9786	10132
2	14144	14472	14506	13948	14351	14515	13496
2	15683	16376	16451	15690	17036	17487	15502
0	25432	24891	24838	19031	19451	19744	
1	20610	21318	21394	20106	20836	21245	18567
4	23295	23983	24056	24092	24926	25190	21967
2	27458	28121	28195	27195	28359	28655	26639
0	53193	53756	53819	49790	50133	50155	

Table 12 Energy levels in reciprocal centimeters for the Pt atom from valence MR-SDCI calculations with the double-zeta basis set, showing the effect of the Breit interaction. Experimental data from Ref. [27]

J	Coulomb	+ Breit	Expt
3	0	0	0
2	766	750	776
4	375	351	824
0	10207	10208	6140
2	6690	6574	6567
3	9316	9068	10117
1	9677	9440	10132
2	13948	13741	13496
2	15690	15433	15502
0	19031	18898	
1	20106	19857	18567
4	24092	23844	21967
2	27195	26798	26639
0	49790	49404	

  - Do not add the fifth *d* primitive (on the grounds that the 5*d* orbital will be used to correlate the 5*s* and 5*p*).
  - Add the fifth and seventh *d* primitives (which results in a loss of about 1 mE_h in the 5*s*5*p* correlation energy). Note that not including the fifth *d* primitive loses 4–8 mE_h correlation energy.
- **Valence plus outer core plus 4*f*:** To the valence plus outer core set, add the fifth and seventh *f* primitives, the seventh, eighth and ninth *d* primitives, the 10th to 12th *p* and *s* primitives, and the core correlating 3*g*2*h*1*i* set. (HF plus 3*s*4*p*4*d*3*f*2*g*1*h* valence plus 3*s*3*p*3*d*2*f*1*g* outer core plus 3*s*3*p*3*d*3*f*3*g*2*h*1*i*; *d* and *f* sets overlap.)

5 Application

The basis sets have been used for calculations on the energy levels of the Pt atom. SCF calculations were performed with the contracted dz, tz, and qz basis sets. MR-SDCI calculations were performed with the $5d^8 6s^2$, $5d^9 6s^1$, and $5d^{10}$ configurations as references. All single and double excitations from the 5*d* and 6*s* orbitals into the virtual space of the SCF calculations were included in the CI calculations. The largest calculation, for $J = 4$ in the qz basis, included about 56,000 CSFs.

The results reported in Table 11 are for two sets of calculations: the valence CI among the three reference configurations and the MR-SDCI calculations. The first set shows the quality of the SCF basis sets. Deviations in relative energies between the dz and tz basis sets range up to 800 cm^{-1}, (0.1 eV, 10 kJ mol^{-1}). Between the tz and qz basis sets, the maximum deviation is an order of magnitude smaller, at 80 cm^{-1} (0.01 eV, 1 kJ mol^{-1}). It is well known that dz basis sets do not provide quantitative accuracy. The MR-SDCI calculations show larger deviations between the basis sets: up to 2000 cm^{-1} between dz and tz, and up to 400 cm^{-1} between tz and qz. Valence correlation clearly improves the prediction of the energy levels for all basis sets, but it is also clear that there are still large discrepancies that must be addressed by correlation of the 5*s* and 5*p* shells, and maybe the 4*f* shell. The Breit interaction contributes a reduction of a few hundred reciprocal centimeters to the excitation energies; results for the dz basis are given in Table 12.

For an application of these basis sets to polarizabilities of PtH_2, AuH and Hg, see Ref. [28].

6 Discussion

The basis sets presented in this paper are intended to form a series for which energy extrapolations [29,30,31] can be performed to obtain higher accuracy. Although the basis sets are not specifically designed for extrapolation, by checking the energy gain as functions are added to the basis set, the principle of adding one function for each existing angular momentum and one function of one unit higher angular momentum as the basis set is enlarged has been adhered to.

It is in fact difficult to determine exponents that are simultaneously optimal for both the SCF energy and the correlation energy. In the qz basis set, for example, the spacing of the three f functions for correlation is larger than that generated by SCF optimization of exponents. Replacing the correlating *f* functions with the SCF functions results in an energy loss of 9 mE_h for Hg and 5 mE_h for Re. After reoptimization of the remaining SCF exponents, the energy loss with respect to the SCF set is 56 μE_h for Hg and 150 μE_h for Re. The energy loss from using the SCF *f* functions in the CI calculations was 1.6 mE_h for Hg. Thus, substituting the *f* functions and reoptimizing the remaining SCF functions is the best compromise.

The alternative to optimizing correlating functions independently, at least for the occupied orbitals, is to construct ANO expansions [32], or atomic natural spinor (ANS) expansions where the spin-dependent terms are included in the SCF. The higher density of the SCF exponents should provide at least as good a correlating ANO set as is obtained from optimizing exponents of primitive functions.

The use of primitive functions for correlation or basis set flexibility creates no problems for methods such as the Douglas–Kroll method. Using primitive functions as an approximation to atomic 4-spinors can cause some problems in correlated four-component calculations, depending on the approach taken to determine the ratio of the large and small components. The prescription used with the NESC method [33] for example, is to use the free-particle ratio. This prescription was used in the MR-SDCI calculations used to optimize exponents. The problem is that some kind of variational collapse can be observed, and the problem is particularly noticeable for *s* functions with larger exponents.

The problem has its roots in the potential used to determine the large and small components—in this case, a zero potential. This potential is not the same as that used to determine the SCF functions. The primitive function with free-particle large to small component ratio is not an eigenfunction of the SCF potential, and therefore is a mix of positive- and negative-energy eigenfunctions of the SCF potential, even though it is an approximation to a positive-energy eigenfunction. When this function is orthogonalized to the SCF functions, the positive-energy components can be projected out to an extent that leaves too much of the negative energy states in the eigenfunction. The effective eigenvalue of the orthogonalized function is now lower than it should be, and it is energetically favorable to occupy this spinor rather than the SCF spinors. The problem is more pronounced for *s* functions because they penetrate to the nucleus and are the most affected by relativity. The most practical alternative is to use ANOs [32] or ANSs, depending on the relativistic Hamiltonian in use.

One further warning is needed in the use of these basis sets. The 5*s* shell is lower in energy than the 4*f* shell. If calculations that include 5*s*5*p* correlation but not 4*f* correlation are performed, selection of the orbitals or spinors to correlate based on the order of the eigenvalues will lead to erroneous results, because one of the 4*f* orbitals will be selected instead of the 5*s* orbital. It is therefore necessary either to reorder the orbitals so that selection of a contiguous range includes the 5*s* and not the 4*f*, or to specify the list of orbitals explicitly to ensure inclusion of the desired orbitals.

The full tables of basis sets including spin-free relativistic SCF [34] 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 approximation recently presented by the author [35].

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 for the construction of various basis sets.

Acknowledgements. The author was supported mainly by Pacific Northwest National Laboratory (PNNL) contract BPNL 291140-A-A3 to Eloret Corporation. This work was supported through the U.S. Department of Energy by the Mathematical, Information, and Computational Science Division phase II grand challenges of the Office of Computational and Technology Research, and was performed under contract DE-AC06-76RLO 1830 with Battelle Memorial Institute. Most calculations were performed on the computing facilities of the Environmental and Molecular Sciences Laboratory of PNNL.

References

1. Pyykkö P (1978) Adv Quantum Chem 11: 353
2. Pyykkö P, Stoll H (2000) Royal Society of Chemistry Specialist Periodical Reports, Chemical Modelling, Applications and Theory 1: 239.
3. (a) Wadt WR, Hay PJ (1985) J Chem Phys 82: 270; (b) Wadt WR, Hay PS (1985) J chme Phys 82: 284; (c) Wadt WR, Hay PS (1985) J chem Phys 82: 299
4. (a) Pacios LF, Christiansen PA (1985) J Chem Phys 82: 2664; (b) Hurley MM, Pacios LF, Christiansen PA, Ross RB, Ermler WC (1986) J Chem Phys 84: 6840; (c) LaJohn LA, Christiansen PA, Ross RB, Atashroo T, Ermler WC (1987) J Chem Phys 87: 2812; (d) Ross RB, Powers JM, Atashroo T, Ermler WC, LaJohn LA, Christiansen PA (1990) J Chem Phys 93: 6654; (e) Ermler WC, Ross RB, Christiansen PA (1991) Int J Quantum Chem (1991) 40: 829; (f) Ross RB, Gayen S, Ermler WC (1994) J Chem Phys 100: 8145
5. (a) Stevens WJ, Basch H, Krauss M (1984) J Chem Phys 81: 6026; (b) Stevens WJ, Krauss M, Basch H, Jasien PG (1992) Can J Chem 70: 612; (c) Cundari TR, Stevens WJ (1993) J Chem Phys 98: 5555
6. Metz B, Schweizer M, Stoll H, Dolg M, Liu W (2000) Theor Chem Acc 104: 22; (b) Metz B, Stoll H, Dolg M (2000) J Chem Phys 113: 2563
7. Christiansen PA (2000) J Chem Phys 112: 10070
8. Osanai Y, Noro T, Miyoshi E (2002) J Chem Phys 117: 9623
9. (a) Dunning TH Jr (1989) J Chem Phys 90: 1007; (b) Kendall RA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96: 6769; (c) Woon DE, Dunning TH Jr (1993) J Chem Phys 98: 1358; (d) Wilson AK, Woon DE, Peterson KA, Dunning TH Jr (1999) J Chem Phys 110: 7667
10. Peterson KA (2003) J Chem Phys 119: 11099
11. Peterson KA, Figgen D, Goll E, Stoll H, Dolg M (2003) J Chem Phys 119: 11113
12. Martin JML, Sundermann A (2001) J Chem Phys 114: 3408
13. Osanai Y, Noro T, Miyoshi E, Sekiya M, Koga T (2004) J Chem Phys 120: 6408
14. Douglas M, Kroll NM (1974) Ann Phys 82: 89
15. (a) Hess BA (1985) Phys Rev A 32: 756; (b) Hess BA (1986) Phys Rev A 33: 3742
16. Nakajima N, Hirao K (2000) J Chem Phys 113: 7786
17. Wolf A, Reiher M, Hess BA (2002) J Chem Phys 117: 9215
18. (a)Tsuchiya T, Abe M, Nakajima T, Hirao K (2001) J Chem Phys 115: 4463; (b) Nakajima T, Hirao K (2002) J Chem Phys 116: 8270
19. Visscher L, Visser O, Aerts PJC, Merenga H, Nieuwpoort WC (1994) Comput Phys Commun 81: 120
20. Saue T, Bakken V, Enevoldsen T, Helgaker T, Jensen HJAa, Laerdahl JK Ruud K, Thyssen J, Visscher L (2000) *Dirac, a relativistic ab initio electronic structure program, release 3.2.* http://dirac.chem.sdu.dk
21. Fægri K Jr (2001) Theor Chem Acc 105: 252
22. (a) Dyall KG (1998) Theor Chem Acc 99: 366; (b) Dyall KG (2002) Theor Chem Acc 108: 365
23. Dyall KG (2002) Theor Chem Acc 108: 335
24. Dyall KG, Fægri K Jr (1996) Theor Chim Acta 94: 39
25. Seth M, Shepard R, Wagner A, Dyall KG (2001) J Phys B 34: 2383
26. Quiney HM, Lærdahl JK, Saue T, Fægri K Jr (1998) Phys Rev A 57: 920
27. Engleman R Jr (1985) J Opt Soc Am B 2: 1934
28. Salek P, Helgaker T, Saue T (2004) Chem Phys, (in press)
29. Feller D (1992) J Chem Phys 96: 6104
30. Martin JML (1996) Chem Phys Lett 259: 669
31. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106: 9639
32. (a)Almlöf J, Taylor PR (1987) J Chem Phys 86: 4070; (b) Almlöf J, Taylor PR (1990) J Chem Phys 92: 551
33. Dyall KG, Enevoldsen T (1999) J Chem Phys 111: 10000
34. Dyall KG (1994) J Chem Phys 100: 2118
35. Dyall KG (2001) J Chem Phys 115: 9136