Theor Chem Acc (2002) 108:335–340
DOI 10.1007/s00214-002-0388-0

Theoretical
Chemistry Accounts

Regular article

Relativistic and nonrelativistic finite nucleus optimized triple-zeta basis sets for the 4*p*, 5*p* and 6*p* elements

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Received: 14 June 2002 / Accepted: 11 August 2002 / Published online: 14 November 2002

Abstract. Relativistic and nonrelativistic valence triple-zeta basis sets have been optimized at the self-consistent-field (SCF) level with a Gaussian nuclear charge distribution for the 4*p*, 5*p* and 6*p* elements. Two *d* and one *f* function were optimized to correlate the valence space, and two *f* and one *g* function were optimized to correlate the $(n-1)d$ shell. In addition, diffuse *s* and *p* functions were optimized at the SCF level and diffuse *d* and *f* functions were optimized at the multireference configuration interaction level for the negative ion. These basis sets are equivalents of the correlation-consistent basis sets. Prescriptions are given for contracting the basis sets.
Electronic supplementary material to this paper can be obtained by using the Springer Link server located at http://dx.doi.org/10.1007/s00214-002-0388-0

Key words: Gaussian basis sets – Relativistic basis sets – *p* block – Triple zeta – Correlating functions

1 Introduction

This paper is the second in a series reporting basis set optimizations for the heavy elements. The first paper presented double-zeta basis sets for the 4*p*, 5*p* and 6*p* elements [1]. These basis sets are adequate for qualitative and semiquantitative calculations, but for higher accuracy, larger basis sets are needed. The first stage in developing larger basis sets is presented in this paper, in which a set of triple-zeta basis sets for the same elements is presented. As for the double-zeta basis sets, they are generated in the style of the correlation-consistent basis sets of Dunning and coworkers [2].

Since the first paper was published, several other basis sets have appeared in the literature, notably a set of better than double-zeta quality family basis sets for most of the periodic table by Fægri [3], and a set of approximately triple-zeta quality for the entire periodic table optimized using the third-order. Douglas–Kroll method by Tsuchiya et al. and Nakajima and Hirao [4]. The development of relativistic basis sets has been reviewed in a recent article by Fægri and the author [5]. The basis sets presented in this paper include not only the self-consistent field (SCF) sets but also polarizing and correlating functions as well. These are vital for describing molecular bonding and must be included in any calculations that hope to achieve quantitative accuracy.

2 Method

The methodology has been described previously [1, 6]. As in the previous paper, ℓ-optimization was employed, and the basis sets were optimized on the average energy of the nonrelativistic p^n configuration, both in the SCF and the configuration interaction (CI) optimizations; the latter are multireference singles and doubles CI (MR-SDCI) optimizations. The procedure followed was the same as that used for the double-zeta basis sets, and is outlined in the following paragraph.

In all the SCF optimizations to determine the basis for the SCF occupied orbitals, the exponents are varied only within a given angular space, i.e. for a given ℓ value, with all other exponents fixed. In a full optimization, the angular spaces are cycled through the optimization process until there is no significant change in the total energy and the gradient with respect to the logarithms of the exponents. The exponents in each angular space are to a large degree independent of the other angular spaces. Convergence of the $\ell > 0$ angular spaces usually only takes two cycles; convergence of the *s* space often takes more because of the larger number of functions and the larger overlaps.

The size of the basis sets was determined by a series of optimizations on the rare-gas atoms. The series was determined by first fully optimizing a reference basis set, then performing optimizations within each angular space for different numbers of exponents with the exponents in the other angular spaces fixed. The criteria of balance between the energy gain in each angular space for the addition of the next function and representation of the outermost maximum of both the *n* and $n-1$ shells were employed to decide on the optimum basis set.

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Extensions to the SCF basis sets were determined in the style of the correlation-consistent basis sets. One diffuse *s* function and one diffuse *p* function were determined in SCF calculations for the negative ion. Valence correlation functions were optimized in MR-SDCI calculations within a $2s2p2d1f$ correlating space. The *s* and *p* correlating functions were taken to be the outermost and the third-outermost functions from the SCF set. These were a little more diffuse than the optimal correlating *s* and *p* functions, but were considered to be adequate for the present purpose. Only the two *d* functions and the *f* function were optimized. Diffuse *d* and *f* functions were optimized for the negative ion in MR-SDCI calculations within a $3s3p3d2f$ correlating space consisting of the valence $2s2p2d1f$ space supplemented by $1s1p1d1f$ diffuse functions, with the diffuse *s* and *p* functions taken from the SCF negative ion optimizations. Correlation functions for the $(n-1)d$ shell were optimized in MR-SDCI calculations in which double excitations out of the *d* shell into a $2f1g$ correlating space were considered. The angular momentum resulting from the coupling of the *d* shell to the correlating functions was constrained to a zero value, so that the correlating configurations represented only *d*-shell correlation.

The CI optimizations were mostly performed with an adaption of the relativistic atomic MRCI program developed by the author [7]. In this adaption, four-spinors consisting of a single Gaussian function with the large and small components determined by diagonalizing the kinetic energy matrix are used as correlating functions in an MRCI calculation. The exponents are optimized using the same second-order algorithm as in the SCF optimization program, with the gradient and Hessian calculated by finite differences.

3 Results

The basis set sizes determined for the $4p$ elements were $23s16p9d$ for the relativistic set and $22s15p9d$ for the nonrelativistic set; for the $5p$ elements the sizes were $28s21p14d$ for the relativistic set and $27s18p13d$ for the nonrelativistic set; and for the $6p$ elements the sizes were $30s26p16d10f$ for the relativistic set and $29s22p15d10f$ for the nonrelativistic set. Total energies for the SCF basis sets of the neutral atoms and the negative ions are compared in Tables 1, 2, and 3 with the numerical limits.

The energies for the nonrelativistic sets are slightly closer to the numerical limit than those for the relativistic sets, with the exception of the $6p$ block. Here, the basis set energy actually goes below the numerical limit. This is not a collapse, because the exponent optimization is variational and the energy is bounded from below; the Hessian in the exponent space is positive-definite at convergence. Rather, this phenomenon has been termed a "prolapse"[3] for the following reason. Any finite basis set represents a projection onto the exact spectrum, and the minimum energy in the projected basis set can fall below the exact energy. If kinetic balance is used between the large and small components, the energy prolapse is of the order of c^{-4}. The energy minimization procedure ensures that, if the variational space is large enough, the energy will fall below the exact energy. This presents a problem for defining a sequence of basis sets whose energy converges on the exact energy. However, the deficiency is in the core and will probably not affect chemical applications. Where it is critical is for properties that are sensitive to the core description [8], 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.

The valence correlating functions are presented in Table 4. For all elements, the largest *d* exponent is a little larger than the smallest *d* exponent from the SCF set. To reduce linear dependence, the smallest SCF *d* exponent should be deleted from the basis set and the two correlating *d* exponents added. The contraction coefficients, which are given in the internet archive (Sect. 5), are derived from SCF calculations where this replace-

Table 1. Total energies in E_h of basis set and numerical self-consistent-field (SCF) calculations and differences between the two for the $4p$ neutral atoms and negative ions

Element		Relativistic		Nonrelativistic	
		Neutral atom	Negative ion	Neutral atom	Negative ion
Ga	Basis	−1942.563114	−1942.550463	−1923.252953	−1923.241329
	Numeric	−1942.563764	−1942.551218	−1923.253477	−1923.241946
	Difference	0.000650	0.000755	0.000524	0.000617
Ge	Basis	−2097.469695	−2097.475549	−2075.330939	−2075.338208
	Numeric	−2097.470361	−2097.476228	−2075.331456	−2075.338739
	Difference	0.000666	0.000679	0.000517	0.000531
As	Basis	−2259.441212	−2259.471704	−2234.161453	−2234.193590
	Numeric	−2259.441912	−2259.472395	−2234.161979	−2234.194109
	Difference	0.000700	0.000691	0.000526	0.000519
Se	Basis	−2428.587526	−2428.647240	−2399.830748	−2399.892279
	Numeric	−2428.588274	−2428.647965	−2399.831290	−2399.892803
	Difference	0.000748	0.000725	0.000542	0.000524
Br	Basis	−2605.022678	−2605.115692	−2572.427456	−2572.522419
	Numeric	−2605.023485	−2605.116465	−2572.428018	−2572.522958
	Difference	0.000807	0.000773	0.000562	0.000539
Kr	Basis	−2788.859751		−2752.038935	
	Numeric	−2788.860624		−2752.039516	
	Difference	0.000873		0.000581	

Table 2. Total energies in E_h of basis set and numerical SCF calculations and differences between the two for the 5*p* neutral atoms and negative ions

Element		Relativistic		Nonrelativistic	
		Neutral atom	Negative ion	Neutral atom	Negative ion
In	Basis	−5880.431288	−5880.423895	−5740.104232	−5740.099382
	Numeric	−5880.431582	−5880.424262	−5740.104531	−5740.099733
	Difference	0.000294	0.000367	0.000299	0.000351
Sn	Basis	−6176.127783	−6176.139559	−6022.841989	−6022.856714
	Numeric	−6176.128089	−6176.139876	−6022.842279	−6022.857017
	Difference	0.000306	0.000317	0.000290	0.000303
Sb	Basis	−6480.518305	−6480.553679	−6313.347671	−6313.386081
	Numeric	−6480.518627	−6480.553998	−6313.347960	−6313.386374
	Difference	0.000322	0.000319	0.000289	0.000293
Te	Basis	−6793.698626	−6793.760902	−6611.674108	−6611.739389
	Numeric	−6793.698968	−6793.761230	−6611.674398	−6611.739676
	Difference	0.000342	0.000328	0.000290	0.000287
I	Basis	−7115.793810	−7115.885919	−6917.886554	−6917.981552
	Numeric	−7115.794175	−7115.886265	−6917.886849	−6917.981838
	Difference	0.000365	0.000346	0.000295	0.000286
Xe	Basis	−7446.895049		−7232.034317	
	Numeric	−7446.895440		−7232.034620	
	Difference	0.000391		0.000303	

Table 3. Total energies in E_h of basis set and numerical SCF calculations and differences between the two for the 6*p* neutral atoms and negative ions

Element		Relativistic		Nonrelativistic	
		Neutral atom	Negative ion	Neutral atom	Negative ion
Tl	Basis	−20274.850300	−20274.842157	−18961.135250	−18961.132268
	Numeric	−20274.850644	−20274.842721	−18961.135824	−18961.132912
	Difference	0.000344	0.000564	0.000574	0.000644
Pb	Basis	−20913.714075	−20913.725487	−19523.260538	−19523.277207
	Numeric	−20913.714332	−20913.725813	−19523.261070	−19523.277785
	Difference	0.000257	0.000326	0.000532	0.000578
Bi	Basis	−21565.705902	−21565.741424	−20094.760892	−20094.800645
	Numeric	−21565.706080	−21565.741649	−20094.761394	−20094.801188
	Difference	0.000178	0.000225	0.000502	0.000543
Po	Basis	−22231.013078	−22231.075755	−20675.673488	−20675.738932
	Numeric	−22231.013179	−22231.075893	−20675.673968	−20675.739446
	Difference	0.000101	0.000138	0.000480	0.000514
At	Basis	−22909.807597	−22909.900037	−21266.032755	−21266.126180
	Numeric	−22909.807616	−22909.900086	−21266.033217	−21266.126674
	Difference	0.000019	0.000049	0.000462	0.000494
Rn	Basis	−23602.104336		−21865.852593	
	Numeric	−23602.104246		−21865.853041	
	Difference	−0.000090		0.000448	

ment has been made. There is in fact very little difference between the nonrelativistic and the relativistic exponents for the 4*p* and 5*p* elements, and it would incur little loss in energy to use the same set in both relativistic and nonrelativistic calculations. For the 6*p* elements, the relativistic exponents are about 10% larger than the nonrelativistic exponents, and the use of the same exponents in both relativistic and nonrelativistic calculations would incur some energy loss. A comparison of nonrelativistic calculations for the rare gases in which the relativistic correlating functions were used in place of the nonrelativistic correlating functions gave energy differences of $15\mu E_h$ for Kr, $70\mu E_h$ for Xe, and $570\mu E_h$ for Rn.

The diffuse functions are presented in Table 5. As for the valence correlating functions, the diffuse functions do not differ much between the relativistic and nonrelativistic sets. The relativistic diffuse functions are a little tighter than the nonrelativistic diffuse functions, with the exception of the *p* functions.

The core correlating functions are presented in Table 6. Again, there is not a big difference between the nonrelativistic and relativistic sets. The exponents from the relativistic sets were used to start the nonrelativistic optimizations. The energy lowering on optimization was only 3–$5\mu E_h$ for the 4*p* elements, increasing to 20–$30\mu E_h$ for the 5*p* elements and 70–$120\mu E_h$ for the 6*p* elements. Clearly, using either set provides results within chemical

Table 4. Correlating 2*d*1*f* functions

Element	Relativistic			Nonrelativistic		
	d	*d*	*f*	*d*	*d*	*f*
Ga	3.14031×10^{-1}	1.08909×10^{-1}	3.17685×10^{-1}	3.05932×10^{-1}	1.06503×10^{-1}	3.08762×10^{-1}
Ge	3.90445×10^{-1}	1.38368×10^{-1}	3.14113×10^{-1}	3.84020×10^{-1}	1.36943×10^{-1}	3.10554×10^{-1}
As	4.78844×10^{-1}	1.73974×10^{-1}	3.79380×10^{-1}	4.71947×10^{-1}	1.72349×10^{-1}	3.73958×10^{-1}
Se	5.74577×10^{-1}	2.12553×10^{-1}	4.62750×10^{-1}	5.66673×10^{-1}	2.10665×10^{-1}	4.56290×10^{-1}
Br	6.77301×10^{-1}	2.53829×10^{-1}	5.61019×10^{-1}	6.67069×10^{-1}	2.51102×10^{-1}	5.52375×10^{-1}
Kr	7.84544×10^{-1}	2.96355×10^{-1}	6.74331×10^{-1}	7.72461×10^{-1}	2.93049×10^{-1}	6.64487×10^{-1}
In	2.39763×10^{-1}	8.86616×10^{-2}	2.66497×10^{-1}	2.26892×10^{-1}	8.52026×10^{-2}	2.48251×10^{-1}
Sn	2.88425×10^{-1}	1.09939×10^{-1}	2.48627×10^{-1}	2.75946×10^{-1}	1.06825×10^{-1}	2.39429×10^{-1}
Sb	3.43297×10^{-1}	1.34930×10^{-1}	2.89885×10^{-1}	3.30389×10^{-1}	1.31774×10^{-1}	2.79835×10^{-1}
Te	4.02284×10^{-1}	1.61787×10^{-1}	3.43785×10^{-1}	3.88493×10^{-1}	1.58545×10^{-1}	3.32639×10^{-1}
I	4.64500×10^{-1}	1.89940×10^{-1}	4.05977×10^{-1}	4.49337×10^{-1}	1.86445×10^{-1}	3.92942×10^{-1}
Xe	5.29597×10^{-1}	2.19067×10^{-1}	4.76724×10^{-1}	5.12785×10^{-1}	2.15222×10^{-1}	4.60914×10^{-1}
Tl	2.46388×10^{-1}	8.99285×10^{-2}	2.97512×10^{-1}	2.04269×10^{-1}	7.87807×10^{-2}	2.32181×10^{-1}
Pb	2.81842×10^{-1}	1.06119×10^{-1}	2.53085×10^{-1}	2.43538×10^{-1}	9.71884×10^{-2}	2.17762×10^{-1}
Bi	3.25040×10^{-1}	1.26580×10^{-1}	2.78626×10^{-1}	2.86745×10^{-1}	1.18292×10^{-1}	2.49257×10^{-1}
Po	3.72051×10^{-1}	1.48635×10^{-1}	3.21913×10^{-1}	3.32558×10^{-1}	1.40751×10^{-1}	2.91441×10^{-1}
At	4.21484×10^{-1}	1.71536×10^{-1}	3.72951×10^{-1}	3.79967×10^{-1}	1.63837×10^{-1}	3.39023×10^{-1}
Rn	4.73002×10^{-1}	1.95078×10^{-1}	4.31009×10^{-1}	4.28739×10^{-1}	1.87278×10^{-1}	3.91677×10^{-1}

Table 5. Diffuse *s*, *p*, *d* and *f* functions

Element	Relativistic				Nonrelativistic			
	s	*p*	*p*	*f*	*s*	*p*	*d*	*f*
Ga	1.73302×10^{-2}	1.05738×10^{-2}	3.35918×10^{-2}	9.48329×10^{-2}	1.72716×10^{-2}	1.07202×10^{-2}	3.31658×10^{-2}	9.35381×10^{-2}
Ge	2.47836×10^{-2}	1.68397×10^{-2}	4.68836×10^{-2}	1.06878×10^{-1}	2.40249×10^{-2}	1.65274×10^{-2}	4.67366×10^{-2}	1.06179×10^{-1}
As	3.12842×10^{-2}	2.24395×10^{-2}	6.25592×10^{-2}	1.40405×10^{-1}	3.08698×10^{-2}	2.24454×10^{-2}	6.23490×10^{-2}	1.38879×10^{-1}
Se	3.77240×10^{-2}	2.78480×10^{-2}	7.99181×10^{-2}	1.88065×10^{-1}	3.74689×10^{-2}	2.77150×10^{-2}	7.97215×10^{-2}	1.86089×10^{-1}
Br	4.40655×10^{-2}	3.31367×10^{-2}	9.92830×10^{-2}	2.60473×10^{-1}	4.35581×10^{-2}	3.28066×10^{-2}	9.59296×10^{-2}	2.55800×10^{-1}
In	1.55272×10^{-2}	9.70088×10^{-3}	2.84752×10^{-2}	8.21985×10^{-2}	1.51120×10^{-2}	1.02359×10^{-2}	2.81975×10^{-2}	7.87864×10^{-2}
Sn	2.10766×10^{-2}	1.46872×10^{-2}	3.84853×10^{-2}	8.74859×10^{-2}	2.04771×10^{-2}	1.50777×10^{-2}	3.81169×10^{-2}	8.51261×10^{-2}
Sb	2.56761×10^{-2}	1.90556×10^{-2}	5.00018×10^{-2}	1.10724×10^{-1}	2.47193×10^{-2}	1.93862×10^{-2}	4.96336×10^{-2}	1.07508×10^{-1}
Te	3.01076×10^{-2}	2.31941×10^{-2}	6.27474×10^{-2}	1.44410×10^{-1}	2.94490×10^{-2}	2.34960×10^{-2}	6.25925×10^{-2}	1.40409×10^{-1}
I	3.50022×10^{-2}	2.72372×10^{-2}	7.69634×10^{-2}	1.97174×10^{-1}	3.38080×10^{-2}	2.74714×10^{-2}	7.71852×10^{-2}	1.91938×10^{-1}
Tl	1.50549×10^{-2}	7.76648×10^{-3}	2.64348×10^{-2}	8.85254×10^{-2}	1.45238×10^{-2}	9.56264×10^{-3}	2.64880×10^{-2}	7.43116×10^{-2}
Pb	2.02344×10^{-2}	1.23676×10^{-2}	3.22036×10^{-2}	8.77664×10^{-2}	1.90274×10^{-2}	1.40033×10^{-2}	3.51349×10^{-2}	7.83356×10^{-2}
Bi	2.45162×10^{-2}	1.62027×10^{-2}	4.32979×10^{-2}	1.06024×10^{-1}	2.31237×10^{-2}	1.77583×10^{-2}	4.51125×10^{-2}	9.67770×10^{-2}
Po	2.81144×10^{-2}	1.97645×10^{-2}	5.59814×10^{-2}	1.35539×10^{-1}	2.70352×10^{-2}	2.13152×10^{-2}	5.62727×10^{-2}	1.24249×10^{-1}
At	3.17280×10^{-2}	2.31267×10^{-2}	6.74341×10^{-2}	1.82392×10^{-1}	3.05429×10^{-2}	2.46149×10^{-2}	6.87129×10^{-2}	1.67866×10^{-1}

accuracy, but it is probably preferable to use the optimized sets for energy extrapolations. For the 6*p* elements, the relativistic exponents are smaller than the nonrelativistic exponents, reflecting the relativistic expansion of the 5*d* shell. The two *f* exponents in the 6*p* set are similar to the outermost two SCF exponents, but are somewhat smaller. However, replacing the SCF exponents with the core-correlating *f* exponents results in a change of several millihartrees in the SCF energy, and using the SCF exponents for core correlation reduces the correlation energy by several millihartrees. No doubt, a larger SCF basis set would have exponents that are much closer to the correlating exponents, but it is not worth increasing the size of the basis set for this purpose. The contraction coefficients given in the internet archive were therefore generated with the SCF set, and for core correlation the two *f* exponents should be added to the basis set.

4 Discussion

There is more of a difference in size between the nonrelativistic and relativistic triple-zeta basis sets than there was for the double-zeta basis sets. For the double-zeta basis sets the influence of the nuclear potential is greater than that of the relativistic corrections; for the triple-zeta basis sets the number of functions is larger, and each function contributes to proportionately less of the energy, and therefore the relativistic effects are relatively more important. Thus, even for the 4*p* elements, an extra *s* and *p* function are needed in the relativistic set to obtain the same energy balance as in the nonrelativistic set. For the 5*p* elements, one more *s*, three more *p* and one more *d* functions are required, and for the 6*p* elements, one more *s*, four more *p* and one more *d* functions are required. As for the double-zeta

Table 6. Core correlating 2*f*1*g* functions

Element	Relativistic			Nonrelativistic		
	f	*f*	*g*	*f*	*f*	*g*
Ga	7.53691	2.10609	4.73594	7.58633	2.12586	4.77361
Ge	8.71519	2.49719	5.48492	8.76586	2.51869	5.52502
As	9.94484	2.90803	6.27408	9.99604	2.93116	6.31633
Se	1.12276	3.33897	7.10287	1.12786×10^{1}	3.36368	7.14700
Br	1.25650	3.79044	7.97131	1.26149×10^{1}	3.81662	8.01698
Kr	1.39583	4.26276	8.87951	1.40060×10^{1}	4.29031	8.92641
In	3.02134	1.00488	2.04007	3.06948	1.02614	2.07139
Sn	3.39106	1.15637	2.29281	3.44245	1.17940	2.32522
Sb	3.77151	1.31218	2.55221	3.82668	1.33718	2.58569
Te	4.16446	1.47294	2.81869	4.22393	1.50010	2.85320
I	4.57121	1.63914	3.09261	4.63551	1.66863	3.12812
Xe	4.99357	1.81160	3.37429	5.06245	1.84314	3.41072
Tl	1.97350	7.08022×10^{-1}	1.51887	2.03493	7.45581×10^{-1}	1.56597
Pb	2.16866	8.02167×10^{-1}	1.67461	2.22817	8.40668×10^{-1}	1.72167
Bi	2.36158	8.95517×10^{-1}	1.83062	2.41987	9.35295×10^{-1}	1.87792
Po	2.55388	9.88739×10^{-1}	1.98757	2.61148	1.03007	2.03528
At	2.74673	1.08233	2.14591	2.80398	1.12541	2.19423
Rn	2.94091	1.17661	2.30605	2.99806	1.22161	2.35511

basis sets, the largest demands of relativity are on the *p* set because of the small component of the $p_{1/2}$. The finite nuclear size places a limit on the maximum exponent needed in the *s* set and therefore it does not grow as rapidly as the *p* set. This is seen in the fact that only two more *s* exponents are required in the 6*p* basis sets than in the 5*p* basis sets, whereas the 5*p* basis sets have five more *s* exponents than the 4*p* basis sets.

The basis sets developed here are designed to follow the pattern of the correlation-consistent basis sets of Dunning and coworkers [2], providing basis sets with the flexibility to correlate the valence space. The recommended procedure for correlating the valence is to uncontract the first and third most diffuse *s* and *p* functions. The correlation energy obtained with optimized *s* and *p* functions is somewhat larger (about 1 millihartree for Xe, for example) but the SCF functions are deemed adequate.

Core correlation is also a consideration, especially in the early members of the *p* block. The optimized *s* and *p* functions are close to the innermost and outermost *s* and *p* SCF functions for the outer core $(n-1)s$ and $(n-1)p$ shells, just as in the valence space, and are a little tighter. The optimized *d* functions are close to the second- and third-outermost SCF functions, with the inner correlating function a little tighter. The recommended procedure is to uncontract the fourth- and sixth-outermost SCF *s* and *p* functions, and a further two *d* functions (the third- and fourth-outermost functions when the outermost *d* function is replaced by the two valence correlation *d* functions).

In the double-zeta basis sets [1], an *f* function was optimized for the static dipole polarization of the $(n-1)d$ shell. The triple zeta basis sets already have *f* functions for both core and valence correlation. Comparison of the polarizing function with the core- and the valence-correlating *f* functions shows that it lies between the two sets. The gap between the valence correlating *f* function and the outermost core-correlating *f* function is large – a factor of about 6–7. For optimal polarization of the *d* shell it may then be necessary to add a function in this gap, either employing the function optimized for the double-zeta set, or taking the geometric mean of the functions on either side of the gap.

The basis sets presented in this and the first paper are intended to form a series for which energy extrapolations [9–11] can be performed to obtain high accuracy. Admittedly, extrapolations from a double-zeta and a triple-zeta set are not very reliable but might give a useful improvement in accuracy over the triple-zeta results themselves. The author's intention is to develop a quadruple-zeta set that could be used for more accurate extrapolations.

The full tables of basis sets including nonrelativistic SCF, spin-free relativistic SCF [12] and Dirac–Fock SCF coefficients are available in ASCII format from the internet archive. 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 [13].

5 Internet archive

This work contains an internet archive in ASCII format. The archive contains the nonrelativistic exponent sets with the coefficients of the Hartree–Fock orbitals and the relativistic exponent sets with the large- and small-component coefficients of the Dirac–Fock spinors and the large Foldy–Wouthuysen transformed large- and small-component coefficients of the spin-free Dirac–Fock spinors, as well as the exponents of the diffuse and the correlating functions. The archive is accessible at no charge at http://dx.doi.org/10.1007/s-00214-002-0388-0.

Acknowledgements. The author was supported by NASA contract NAS2-14031 and Pacific Northwest National Laboratory (PNNL) contract BPNL 291140-A-A3 to Eloret. 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 performed under contract DE-AC06-76RLO 1830 with Battelle Memorial Institute. The calculations were performed on the IBM RS6000 workstations of the Computational Chemistry Branch at NASA Ames Research Center, on the Sun and IBM RS6000 workstations of the Theory, Modeling and Simulations group of the Environmental and Molecular Sciences Laboratory of PNNL, and on the IBM SP computer at the Environmental and Molecular Sciences Laboratory of PNNL.

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