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REGULAR ARTICLE

Kenneth G. Dyall

Relativistic quadruple-zeta and revised triple-zeta and double-zeta basis sets for the 4p, 5p, and 6p elements

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Abstract Relativistic basis sets of quadruple-zeta quality have been optimized at the self-consistent field (SCF) level with a Gaussian nuclear charge distribution for the 4p, 5p and 6p elements. To these sets, a valence correlating 3d2f1g set was optimized in multireference CI calculations on the valence p^n states, and a correlating 3f2g1h set was optimized on the same states, to correlate the $(n-1)$d shell. The SCF d sets were reoptimized with the valence correlating d set included in the SCF calculation and held fixed. The d sets of the double-zeta and triple-zeta basis sets reported previously were also reoptimized in this manner, and a larger s set was introduced into the double-zeta basis sets for the 5p elements. Likewise, the SCF f sets for the 6p elements were reoptimized with the valence correlating f functions added and held fixed. Prescriptions are given for constructing contracted basis sets. The basis sets are available as an internet archive and from the Dirac program web site, http://dirac.chem.sdu.dk.

Keywords Gaussian basis sets · Relativistic basis sets · p-block elements · Quadruple zeta · Correlating functions

1 Introduction

Since calculations on molecules containing heavy elements using all-electron relativistic methods have become more popular, a demand for appropriate basis sets has arisen. Several groups are working actively on this issue, and have published a number of basis sets [1–14]. However, most of the the basis sets developed do not include polarization, diffuse, or correlating functions. This deficiency has been remedied in part by Osanai et al., with their contracted correlating sets [15–17], by Fægri [7], via determination of optimal MP2 energies in an even-tempered set, and by the author [8–11], in the style of the correlation-consistent basis sets [18–21]. The development of relativistic basis sets has been reviewed in a recent article by Fægri and the author [22].

Basis set development for the heavy elements has not been limited to all-electron methods. There are a number of basis sets now becoming available for effective core potentials or pseudopotentials [23–27] and model potentials [15–17] that include correlating functions.

This paper is the fourth in a series reporting basis set optimizations for the heavy elements. The goal of this series is to provide relativistically optimized basis sets of double-zeta, triple-zeta, and quadruple-zeta quality, including correlating functions for the valence and outer core, diffuse functions, and dipole polarization functions. The first paper presented double-zeta basis sets for the 4p, 5p and 6p elements [8]. These basis sets are adequate for qualitative and semi quantitative calculations, but for higher accuracy, larger basis sets are needed. The second presented triple-zeta basis sets for the same elements [10], while a third paper presented double-zeta, triple-zeta, and quadruple-zeta basis sets for the 5d elements [11]. In this paper, the series of basis sets for the p-block elements is completed with quadruple-zeta basis sets, and revisions to the double-zeta and triple-zeta basis sets are presented, based on experience gained from ongoing basis set development.

2 Methods

The methods used have been described previously [8,10,28, 29]. The basis sets are optimized in Dirac–Hartree–Fock calculations using the Dirac Hamiltonian. As for the previous basis sets, ℓ-optimization was employed. In the SCF optimizations, the exponents are varied only within a given angular space, i.e. for a given ℓ value, with all other exponents fixed. The exponents in each angular space are to a large degree independent of those in the other angular spaces. The angular spaces are cycled through the optimization process until there is no significant change in the total energy and the gradient with respect to the logarithms of the exponents. Usually only two cycles are required.

K.G. Dyall
Schrödinger, Inc., 101 SW Main Street, Suite 1300,
Portland, OR 97204, USA
E-mail: dyall@schrodinger.com

For example, for Tl, the starting basis set is taken from Pb. The s exponents are optimized with the p and d exponents fixed. Likewise, the p exponents are optimized with the s and d exponents fixed, and the d exponents are optimized with the s and p exponents fixed. The optimized exponents from all three calculations are then combined to form a new starting set, and the s exponents, the p exponents, and the d exponents are again optimized in three separate calculations with all other exponents fixed.

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.

Extensions to the SCF basis sets were determined in the style of the correlation consistent basis sets [16–21]. Valence correlation functions were optimized in MR-SDCI calculations on the average energy of the valence s^2p^n states within a 3s3p3d2f1g correlating space. The s and p correlating functions were taken to be the first, third, and fourth outermost functions from the SCF set. Subsequent MR-SDCI calculations showed that there is only a small amount of variation due to different choices of the s and p correlating functions. One diffuse s function and one diffuse p function were determined in SCF calculations for the negative ion. Diffuse d, f, and g functions were optimized for the negative ion in MR-SDCI calculations within a 4s4p4d3f2g correlating space consisting of the valence 3s3p3d2f1g space supplemented by a 1s1p1d1f1g diffuse set, with the diffuse s and p functions taken from the SCF negative ion optimizations and held fixed. Correlating functions for the $(n - 1)$d shell were optimized in MR-SDCI calculations in which double excitations out of the d shell into a 3f2g1h correlating space were included. 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 performed with an adaption of RAMCI, a Relativistic Atomic Multireference Configuration Interaction program developed by the author [24]. In this adaption, 4-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 a multireference CI 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.

Following the optimization of the valence correlating functions, the d sets were reoptimized with the outermost two functions replaced by the three functions from the correlating set, which were held fixed. The f set for the 6p elements was also reoptimized with the two correlating f functions added and held fixed. In this way, a single exponent set is obtained. This procedure represents a compromise for the correlating f functions for the 5d shell in the 6p elements, because of the overlap with the occupied 4f. Replacement correlating f functions for the 5d were determined by performing the same MR-SDCI calculations as used for optimizing the correlating f functions, but varying the selection of f exponents used for correlation.

To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed 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. 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 functions to the DHF occupied functions. For the valence space it was found necessary to perform the MR-SDCI calculations for all elements because of the variation in correlation energy across the rows. For the correlation of the $(n - 1)$d there was little variation from the early part of the block to the later part, so calculations were performed only for a selection of elements.

MRCI calculations on the spin–orbit splitting of Tl have been carried out to demonstrate the validity of the basis sets, using the RAMCI program.

3 Primitive basis sets

The SCF basis set sizes chosen for the quadruple zeta basis were 30s21p12d for the 4p block, 33s27p17d for the 5p block, and 34s31p20d12f for the 6p block. After replacement of the outer two d functions with the valence correlating d set for all elements, and addition of the valence correlating f set to the 6p elements, the reoptimized basis sets are 30s21p13d for the 4p block, 33s27p18d for the 5p block, and 34s31p21d14f for the 6p block.

The s set for the 6p block has only one more function than the s set for the 5p. In all the other angular spaces, the increase from 4p to 5p to 6p is several functions. There are several factors in this apparently anomalous behavior. The finite nucleus imposes a maximum size on the largest exponent in the basis set. The nuclear radius increases with Z, and the maximum exponent correspondingly decreases. So, for example, the largest s exponent for Xe is about 8×10^7, but for Rn it is 6×10^7. This phenomenon was first noted by Visser et al. [30]. Combined with this limit, the decrease in the radial extent of the spinors means that there are fewer functions needed to describe the 1s function. The extent of the 1s function can be marked by the change in sign of the coefficients in the 2s spinor. This change occurs after 16 functions for Rn, but after 18 functions for Xe, and the exponent before the change is three times larger in Rn than in Xe. A third factor is that the mean radius of the 5s in Xe is almost the same as the mean radius of the 6s in Rn, due to both relativistic

Table 1 Total energies in E_h of quadruple-zeta basis set and numerical SCF calculations and differences between the two for the 4p neutral atoms and negative ions

	Neutral atom	Negative ion
Ga		
Basis	−1942.563744	−1942.551159
Numeric	−1942.563764	−1942.551218
Difference	0.000020	0.000059
Ge		
Basis	−2097.470340	−2097.476204
Numeric	−2097.470361	−2097.476228
Difference	0.000021	0.000024
As		
Basis	−2259.441891	−2259.472365
Numeric	−2259.441912	−2259.472395
Difference	0.000021	0.000030
Se		
Basis	−2428.588245	−2428.647937
Numeric	−2428.588274	−2428.647965
Difference	0.000029	0.000028
Br		
Basis	−2605.023461	−2605.116442
Numeric	−2605.023485	−2605.116465
Difference	0.000024	0.000023
Kr		
Basis	−2788.860597	
Numeric	−2788.860624	
Difference	0.000027	

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

	Neutral atom	Negative ion
In		
Basis	−5880.431579	−5880.424228
Numeric	−5880.431582	−5880.424262
Difference	0.000003	0.000034
Sn		
Basis	−6176.128087	−6176.139870
Numeric	−6176.128089	−6176.139876
Difference	0.000002	0.000006
Sb		
Basis	−6480.518627	−6480.553997
Numeric	−6480.518627	−6480.553998
Difference	0.000000	0.000001
Te		
Basis	−6793.698968	−6793.761232
Numeric	−6793.698968	−6793.761230
Difference	0.000000	−0.000002
I		
Basis	−7115.794178	−7115.886268
Numeric	−7115.794175	−7115.886265
Difference	−0.000003	−0.000003
Xe		
Basis	−7446.895444	
Numeric	−7446.895440	
Difference	−0.000004	

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

	Neutral atom	Negative ion
Tl		
Basis	−20274.851084	−20274.843085
Numeric	−20274.850644	−20274.842721
Difference	−0.000440	−0.000364
Pb		
Basis	−20913.714794	−20913.726266
Numeric	−20913.714332	−20913.725813
Difference	−0.000462	−0.000453
Bi		
Basis	−21565.706648	−21565.742217
Numeric	−21565.706080	−21565.741649
Difference	−0.000568	−0.000568
Po		
Basis	−22231.013820	−22231.076534
Numeric	−22231.013179	−22231.075893
Difference	−0.000641	−0.000641
At		
Basis	−22909.808337	−22909.900808
Numeric	−22909.807616	−22909.900086
Difference	−0.000721	−0.000722
Rn		
Basis	−23602.105077	
Numeric	−23602.104246	
Difference	−0.000821	

contraction of the s spinors and the lanthanide contraction. This means that the s functions between the 1s and the ns must fit into essentially the same space, and the functions in Rn are more compressed than those in Xe.

Total energies of the neutral atoms and the negative ions for the reoptimized SCF basis sets are compared in Tables 1, 2, and 3 with the numerical limits. As for the 5d elements, the energies for the 6p elements are lower than the numerical energies. In addition, the energies for some the 5p elements go below the exact energy by a small amount. This is because the lower bound on the energy for the exponent optimization is lower than the exact energy by order c^{-4} — a phenomenon known as "prolapse" [6]. This is not a variational collapse because there is a lower bound: the bound is simply not the exact energy. To obtain the exact energy, the relation between the large- and small-component primitive basis functions would have to go beyond the kinetic balance prescription [31]. This problem probably matters only for properties that are sensitive to the details of the wave function near the nucleus [32], and for these properties an even-tempered set covers the space better.

The selection of a p set for the 6p elements is complicated by the spin–orbit splitting. At the beginning of the block, the four smallest exponents are shared by the $6p_{1/2}$ and the $6p_{3/2}$. By the end of the block, the main contributions to the outer maximum of the $6p_{1/2}$ come from the second through the fifth smallest exponents, whereas for the outer maximum of the $6p_{3/2}$ the first through the fourth smallest exponents are the main contributors. The coefficients for the five smallest functions are shown in Table 4. This kind of change did not happen for the dz and tz basis sets because the energy changes with the variation in exponents is larger and the spacing of the exponents is larger. There is, nevertheless, a difference in the coefficient sizes in the dz and tz basis sets due to the spin-orbit effect.

The exponents of the valence correlating 3d2f1g functions are presented in Table 5, and the exponents of the core

Table 4 Coefficients of the outermost five p functions for the 6p block

	Tl	Pb	Bi	Po	At	Rn
$6p_{1/2}$						
	−0.0033	−0.0329	0.0322	0.0144	0.0559	0.0701
	0.2516	0.2744	0.3567	0.3820	0.4085	0.4277
	0.4547	0.4784	0.4732	0.4870	0.4721	0.4686
	0.3722	0.3524	0.2740	0.2559	0.2325	0.2177
	0.0767	0.0632	0.0371	0.0303	0.0253	0.0219
$6p_{3/2}$						
	−0.0736	−0.1037	−0.0627	−0.0908	−0.0643	−0.0617
	0.1428	0.1643	0.2443	0.2589	0.2888	0.3059
	0.3976	0.4298	0.4540	0.4732	0.4693	0.4728
	0.4594	0.4394	0.3791	0.3685	0.3505	0.3404
	0.1719	0.1486	0.1061	0.0967	0.0888	0.0835

correlating 3f2g1h functions are presented in Table 6. The diffuse 1s1p1d1f1g set is presented in Table 7.

The revision of the tz basis sets consisted entirely of the reoptimization of the d and f exponents after addition of the valence correlating set. For the d sets, the smallest exponent was replaced by the two valence correlating exponents. For the f set in the 6p block, the two smallest exponents were replaced by the core correlating f exponents. The final basis set sizes including the d valence correlating functions are 23s16p11d for the 4p block, 28s21p15d for the 5p block, and 30s26p17d10f for the 6p block.

In addition to the reoptimization of the d sets, the revision of the dz basis sets included a change from 19s to 21s for the 5p block. This larger s set is more in keeping with the basis sets for the other p blocks and with the increase in size from dz to tz to qz. The final basis sets now include the d valence correlating function, to give basis set sizes of 15s11p7d for the 4p block, 21s15p11d for the 5p block, and 24s20p14d8f for the 6p block.

These reoptimized basis sets are available as an internet archive and from the Dirac web site, http://dirac.chem.sdu.dk.

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 adding primitive functions to the SCF occupied spinor or orbital set. Two primary contraction patterns are described: a valence basis set, which correlates the *n*s and *n*p orbitals; and a valence + outer core set which adds functions for $(n-1)$d correlation to the valence set. To any of these contractions, the relevant diffuse functions listed in Table 7 can be added.

Determining the best primitives to uncontract so as to maximize the correlation energy was not a trivial task for the qz basis sets. Martin and Sundermann [25] found some variation in the optimum exponent set in their basis sets. Also, for the qz basis sets, the correlation of the second outermost radial maximum becomes more important, as the correlation of the outermost radial maximum is saturated. In the final basis set, however, a balance must be struck between correlation and valence flexibility.

In all three rows, the choice of the best three s functions lay between two sets: the first, second, and fourth (denoted s124), and the third, fourth, and fifth (denoted s345). (The functions are counted in increasing exponent size from the smallest.) The variation in correlation energy between these two sets was no more than $64\mu E_\mathrm{h}$. The s124 set was chosen because it provides better valence flexibility.

In the p space, the best set of three p functions was the third, fourth, and fifth (p345), with one exception, for Sn. Unlike the s space, there was no single set that was consistently close to this set. All sets of three of the outer four functions lay within a few hundred microhartrees of each other, and the gap between these and the p345 set increased with Z across each row. Any choice for valence flexibility compromises the valence correlation, by up to 1 $\mathrm{m}E_\mathrm{h}$.

Correlation is not the only concern, however. The contraction pattern just described does not completely address the valence flexibility issue, for which two of the outermost three functions should probably be uncontracted. Ultimately, to obtain accurate results that are worth extrapolating, both core and valence correlation must be included. It is, therefore, acceptable to make some compromise on either, provided the best set is included, or at least a set that does not introduce too much error. With this principle, any valence set that includes the third and fourth p functions, combined with a core set that includes the fifth p function would cover the p345 set for valence correlation.

In the descriptions below, 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. The primitives are to be taken from the SCF set, which include the valence correlating d and f functions, where appropriate.

4.1 The 4p block

Valence: To the SCF functions, add the first, second, and fourth s primitives, the first, third, and fourth p primitives, the first through third d primitives (the correlating *d* functions), and the 2f1g functions from the valence correlating set.
(HF + 3s3p3d2f1g valence)
Valence + outer core: To the valence set add the fifth, sixth, and seventh s and p primitives, the fourth, sixth, and seventh d primitives, and the core correlating 3f2g1h set.
(HF + 3s3p3d2f1g valence + 3s3p3d3f2g1h outer core)

4.2 The 5p block

Valence: To the SCF functions, add the first, second, and fourth s primitives, the first, third, and fourth p primitives, the first through third d primitives (the correlating d functions), and the 2f1g functions from the valence correlating set.
(HF + 3s3p3d2f1g valence)

Table 5 Exponents of valence correlating 3d2f1g functions for the quadruple-zeta basis sets

Element	d	d	d	f	f	g
Ga	4.31414E − 01	2.09574E − 01	8.31208E − 02	4.90073E − 01	2.04131E − 01	4.18123E − 01
GE	5.22133E − 01	2.52827E − 01	1.03880E − 01	5.08270E − 01	1.88573E − 01	4.52867E − 01
As	6.30122E − 01	3.13728E − 01	1.31060E − 01	5.95325E − 01	2.27300E − 01	5.01829E − 01
SE	7.46981E − 01	3.83603E − 01	1.61868E − 01	7.04177E − 01	2.78907E − 01	5.72879E − 01
Br	8.70267E − 01	4.59929E − 01	1.95251E − 01	8.26947E − 01	3.41663E − 01	6.57431E − 01
Kr	9.99547E − 01	5.42127E − 01	2.30943E − 01	9.61766E − 01	4.18638E − 01	7.51237E − 01
In	3.41626E − 01	1.84821E − 01	7.26728E − 02	4.00472E − 01	1.70976E − 01	3.42677E − 01
Sn	3.95454E − 01	2.15734E − 01	8.83342E − 02	3.99548E − 01	1.51528E − 01	3.57816E − 01
Sb	4.61537E − 01	2.61885E − 01	1.08788E − 01	4.50109E − 01	1.76261E − 01	3.82471E − 01
TE	5.31938E − 01	3.14870E − 01	1.31570E − 01	5.15526E − 01	2.09779E − 01	4.23231E − 01
I	6.05033E − 01	3.72517E − 01	1.55801E − 01	5.88275E − 01	2.50201E − 01	4.73130E − 01
XE	6.77357E − 01	4.31727E − 01	1.80474E − 01	6.65710E − 01	2.99535E − 01	5.28684E − 01
Tl	3.67839E − 01	1.97031E − 01	7.46000E − 02	4.34585E − 01	1.84851E − 01	3.71719E − 01
Pb	4.02082E − 01	2.14896E − 01	8.54398E − 02	4.12384E − 01	1.51905E − 01	3.72401E − 01
Bi	4.47149E − 01	2.46379E − 01	1.00172E − 01	4.47623E − 01	1.75081E − 01	3.80942E − 01
Po	5.06981E − 01	2.90486E − 01	1.19141E − 01	4.93276E − 01	1.98197E − 01	4.04618E − 01
At	5.71596E − 01	3.37614E − 01	1.38925E − 01	5.47768E − 01	2.31051E − 01	4.39719E − 01
Rn	6.46214E − 01	3.89532E − 01	1.60155E − 01	6.05050E − 01	2.71498E − 01	4.80567E − 01

Table 6 Exponents of core correlating 3f2g1h functions for the quadruple-zeta basis sets

Element	f	f	f	g	g	h
Ga	1.22480E + 01	4.13113E + 00	1.39235E + 00	8.49733E + 00	2.70975E + 00	5.42526E + 00
Ge	1.41607E + 01	4.85873E + 00	1.68461E + 00	9.82558E + 00	3.20854E + 00	6.29850E + 00
As	1.61450E + 01	5.61650E + 00	1.99098E + 00	1.12147E + 01	3.73317E + 00	7.21665E + 00
Se	1.82069E + 01	6.40664E + 00	2.31219E + 00	1.26662E + 01	4.28396E + 00	8.17986E + 00
Br	2.03504E + 01	7.23060E + 00	2.64874E + 00	1.41813E + 01	4.86136E + 00	9.18848E + 00
Kr	2.25786E + 01	8.08954E + 00	3.00103E + 00	1.57614E + 01	5.46573E + 00	1.02429E + 01
In	4.56172E + 00	1.83190E + 00	7.22085E − 01	3.03282E + 00	1.20819E + 00	2.34037E + 00
Sn	5.25231E + 00	2.12818E + 00	8.55202E − 01	3.37233E + 00	1.38465E + 00	2.63459E + 00
Sb	6.03497E + 00	2.44816E + 00	9.95627E − 01	3.71690E + 00	1.56501E + 00	2.93676E + 00
Te	6.94341E + 00	2.79719E + 00	1.14495E + 00	4.06794E + 00	1.74990E + 00	3.24762E + 00
I	8.02111E + 00	3.18008E + 00	1.30447E + 00	4.42632E + 00	1.93971E + 00	3.56761E + 00
Xe	9.31703E + 00	3.59951E + 00	1.47483E + 00	4.79265E + 00	2.13467E + 00	3.89682E + 00
Tl	2.62242E + 00	1.20078E + 00	5.02349E − 01	2.18903E + 00	8.97006E − 01	1.69419E + 00
Pb	2.85287E + 00	1.34515E + 00	5.79437E − 01	2.38274E + 00	1.00851E + 00	1.87149E + 00
Bi	3.07888E + 00	1.48801E + 00	6.55663E − 01	2.57432E + 00	1.11913E + 00	2.04857E + 00
Po	3.30316E + 00	1.63085E + 00	7.31829E − 01	2.76539E + 00	1.22968E + 00	2.22627E + 00
At	3.52795E + 00	1.77480E + 00	8.08508E − 01	2.95704E + 00	1.34070E + 00	2.40521E + 00
Rn	3.75343E + 00	1.91980E + 00	8.85746E − 01	3.15004E + 00	1.45256E + 00	2.58583E + 00

Table 7 Exponents of diffuse 1s1p1d1f1g functions for the quadruple-zeta basis sets

Element	s	p	d	f	g
Ga	1.43951E − 02	8.37490E − 03	2.65498E − 02	6.46165E − 02	1.65550E − 01
Ge	2.05105E − 02	1.37177E − 02	3.64866E − 02	6.68910E − 02	1.82622E − 01
As	2.63040E − 02	1.84298E − 02	4.81977E − 02	8.87179E − 02	2.18444E − 01
Se	3.09295E − 02	2.29359E − 02	6.08413E − 02	1.21981E − 01	2.64189E − 01
Br	3.79754E − 02	2.73861E − 02	7.46061E − 02	1.89006E − 01	3.16365E − 01
In	1.24203E − 02	8.04303E − 03	2.39660E − 02	5.58983E − 02	1.39331E − 01
Sn	1.76513E − 02	1.23810E − 02	3.18999E − 02	5.55347E − 02	1.49230E − 01
Sb	2.23122E − 02	1.59726E − 02	4.09333E − 02	7.13556E − 02	1.73455E − 01
Te	2.75395E − 02	1.92004E − 02	5.04211E − 02	9.70911E − 02	2.05034E − 01
I	3.20971E − 02	2.24758E − 02	6.03152E − 02	1.48746E − 01	2.41631E − 01
Tl	1.14776E − 02	5.86407E − 03	2.19190E − 02	5.80388E − 02	1.55972E − 01
Pb	1.73210E − 02	9.99471E − 03	2.46831E − 02	5.39821E − 02	1.54183E − 01
Bi	2.10260E − 02	1.27388E − 02	3.36615E − 02	6.90011E − 02	1.71433E − 01
Po	2.28227E − 02	1.59381E − 02	4.50365E − 02	8.97800E − 02	1.97231E − 01
At	2.74709E − 02	1.84208E − 02	5.35478E − 02	1.31430E − 01	2.29661E − 01

Valence + outer core: To the valence set add the fivth, sixth, and eighth s primitives, the sixth, seventh, and eighth p primitives, the fifth, sixth, and seventh d primitives, and the core correlating 3f2g1h set.
(HF + 3s3p3d2f1g valence + 3s3p3d3f2g1h outer core.)

4.3 The 6p block

Valence: To the SCF functions, add the first, second, and fourth s primitives, the second, third, and fourth p primitives, the first through third d primitives (the correlating d functions), the first and second f primitives (the correlating f functions), and the valence correlating g function.
(HF + 3s3p3d2f1g valence)
Valence + outer core: To the valence set add the fifth, sixth, and eighth s primitives, the sixth, seventh, and eighth p primitives, the fifth, sixth and seventh d primitives, the third, fourth and fifth f primitives, and the 2g1h functions from the outer core correlating set.
(HF + 3s3p3d2f1g valence + 3s3p3d3f2g1h outer core)

5 Applications

To test the basis sets, a series of CI calculations was performed on the Tl atom. The spin–orbit splitting of the Tl atom has been the subject of several investigations [33–36]. The experimental value is 7793 cm^{-1}. The results for valence correlation with the dz, tz, and qz basis sets are given in Table 8. The DHF calculations include only the $6s^2 6p^1$ configuration. The calculations marked "Ref" include the $6p^3$ configuration, which causes a significant decrease in the spin–orbit splitting. This space was the reference space in the subsequent CI calculations. Including single and double excitations (CISD) increases the spin–orbit splitting by an amount that increases with basis set size. Triple excitations have very little effect on the splitting, and are ignored in subsequent calculations. Clearly, valence correlation is insufficient to reproduce the experimental value. Addition of the Breit interaction cannot make up the difference: in fact, it makes the splitting smaller by about 140 cm^{-1}.

Table 8 Spin–orbit splitting of the Tl atom as a function of basis set and valence correlation

Method	dz	tz	qz
DHF	7759.96	7642.30	7639.88
Ref	7138.53	6977.81	6974.07
CIS	7196.45	7063.26	7055.23
CISD	7240.53	7181.73	7206.75
CISDT	7239.12	7178.50	7203.25

Table 9 Spin–orbit splitting of the Tl atom as a function of core configurations added, in a dz basis set. Each row in the table represents the addition of the specified class of configurations to the calculation presented in the previous row. The reference calculation is the calculation designated Ref in Table 8

Configurations added	5d corr.	5d+5p corr.
Internals	7059.26	7055.50
Valence singles + doubles	7220.17	7215.97
Core singles	7242.91	7252.66
Core–valence doubles	7338.44	7405.39
Core doubles	7599.44	7729.33

The bulk of the discrepancy is made up by correlating the 5d shell and the 5p shell, as indicated by the results in Table 9. In this table, "internals" include single and double excitations from the designated core shells into the valence space, which comprises the 6s, $6p_{1/2}$ and, $6p_{3/2}$ spinors. The remaining excitations are to the external (correlating) space. The "core singles" excitations represent core polarization; the core–valence doubles consist of excitation of one core electron and one valence electron into the external space, while core doubles are excitations of two electrons from the core into the external space. The enlargement of the correlating space with functions that describe outer core correlation also makes up for some of the deficiency in the valence correlation due to the small size of the dz basis set. The best value in the dz basis set is still smaller than experiment, and will be further reduced by the Breit interaction. The remaining discrepancy with experiment comes from increasing the size of the correlating space, as shown by calculations including 5d core–valence correlation (but not core–core correlation) with a triple-zeta basis set, which yield a value of 7,913 cm^{-1} for the splitting.

The effects on the spin–orbit splitting can be rationalized by the effective screening of the 6p spinors. Internal excitations (those between occupied orbitals) reduce the splitting because although they create core holes, they increase the repulsion in the 6p shell and, therefore, increase the direct screening of the 6p by other 6p electrons. Valence correlation moves a certain amount of 6s density into virtual spinors, and reduces the screening, thereby increasing the spin–orbit splitting. Likewise, core correlation moves core density into virtual spinors and reduces the screening. Angular correlation is important because it removes density from the region near the nucleus, where relativistic effects are largest.

6 Internet Archive

The full tables of basis sets including spin-free relativistic SCF [37] and Dirac–Fock SCF coefficients are available in ASCII format from the Dirac web site, http://dirac.chem.sdu.dk, and as an 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, NESC1e [38]. The correlating, polarizing, and diffuse functions are included, and prescriptions are given for the construction of various contracted basis sets.

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