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Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 4d elements Y–Cd

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Abstract Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized for the 4d elements Y–Cd. The basis sets include SCF exponents for the occupied spinors and for the 5p shell; exponents of correlating functions for the valence shell, the 4s and 4p shells, and the 3d shell; and exponents of functions for dipole polarization of the 4d 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 and from the Dirac program web site, http://dirac.chem.sdu.dk.

Keywords Relativistic basis set · 4d Elements · Gaussian functions · Double zeta · Triple zeta · Quadruple zeta · Correlating functions

1 Introduction

With the increasing speed of computers and the development of methodology, all-electron relativistic calculations on heavy-element compounds can now be performed routinely. The main hindrance to such calculations is now the lack of basis sets. Several groups are actively working on the development of basis sets that include relativistic effects, either via the Dirac–Coulomb Hamiltonian [1–14] or the Douglas-Kroll-Hess [15–17] Hamiltonian [18–24]. Many of these do not include functions for correlation. This paper is one of a series of papers [5–10] presenting relativistic basis sets optimized with the Dirac–Coulomb Hamiltonian that include

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diffuse functions and valence and outer core correlating functions in addition to the SCF sets. One of the goals of the present series is to provide basis sets in the style of the correlation-consistent basis sets [25–28] that give fairly uniform quality across the lower portion of the periodic table.

This paper reports relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 4d elements Y–Cd. The challenge of providing consistent basis sets for this block lies in the variable occupation of the 5s, which is zero for Pd, two for Y, Zr, Tc, and Cd, and one for the remaining elements. In addition to the SCF sets, which include functions to describe the 5p shell, the basis sets include high angular momentum correlating functions for the 4d shell, the 4s and 4p shells, and the 3d shell, and functions for dipole polarization of the 4d 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 [5–7,29,30]. The basis sets are optimized in Dirac–Hartree–Fock calculations using the Dirac–Coulomb Hamiltonian with the standard Gaussian nuclear charge distribution [31]. As for the previous basis sets, ℓ-optimization was employed. The s exponents were optimized on the average energy of the ground configuration, except for Pd where the d^9s^1 configuration was used. Exponents for the SCF occupied p functions (2p–4p) were optimized on the average energy of the ground configuration. Functions were then added for the 5p shell and the exponents that describe the outermost maxima of the 3p, 4p and 5p shells were reoptimized

on the average energy of the $d^n p^2$ configuration. The d exponents were optimized on the average energy of the ground configuration.

The basis set sizes were selected for consistency with the 5p basis sets [8], taking into account energy balance and the distribution of exponents among the maxima of all the orbitals. The designations "double zeta", "triple zeta" and "quadruple zeta" refer to the representation of the outermost maxima of the s and p orbitals, as explained in [9]. To maintain energy balance, the representation of the outermost maximum of the 4d orbital takes two extra functions: four for dz, five for tz, and six for qz.

Correlating functions were optimized in MR-SDCI calculations on the ground configuration, using the RAMCI program [30] modified for basis set optimization. All states of this configuration, weighted by their J value, were included in the optimization. This reference set was used in all correlating function optimizations.

For the valence 4d and 5s shells, the correlating function spaces were 1f for the dz basis set, 2f1g for the tz basis set, and 3f2g1h for the qz basis set. All single and double excitations out of the 4d and 5s orbitals were included in the CI expansion.

Functions for correlation of the 4s and 4p shells were optimized for the tz and qz basis sets. The correlating spaces were 2s2p2d1f for tz and 3s3p3d2f1g for qz. All single and double excitations out of the 4s and 4p shells that couple to $J = 0$ were included in the CI expansion. The s, p, and d functions were taken from the SCF set. For the dz basis set, there was no need to optimize functions because the correlating d function can be taken from the SCF set.

To match the 5d basis sets, correlating functions were optimized for the next innermost shell, i.e., the 3d shell. Since the 3d shell lies much deeper for the 4d elements than the 4f for the 5d, it is unlikely that these correlating functions will be needed for any but the highest accuracy calculations. The 3d correlating function spaces were 1f for the dz basis set, 2f1g for the tz basis set, and 3f2g1h for the qz basis set. Only those double excitations out of the 3d shell that coupled to $J = 0$ were included in the CI expansion.

Functions for dipole polarization of the 4d shell were determined as follows. For the dz basis sets, a single f function was determined by maximizing the polarizability calculated by second-order perturbation theory. The basis states for the perturbation theory consisted of the eigenfunctions of the Dirac Hamiltonian for the configurations generated by a single d→f excitation. For the tz basis sets, the correlating f set overlaps the dipole polarizing f set for the dz basis set for part of the row. The correlating f set was therefore extended in an even-tempered sequence to produce a diffuse f function. The ratio used was the ratio of the correlating f functions. A diffuse g function was determined by applying the same ratio 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.

The contraction coefficients for the SCF occupied orbitals were obtained from calculations on a weighted average of the $d^n s^2$, $d^{n+1} s^1$, and $d^n p^2$ configurations. The individual CSF in each configuration were weighted by their degeneracy $(2J + 1)$. The weights were then scaled so that the weights of each of the above configurations were in the ratio 6:3:1 for Y, Zr, and Tc where the s is doubly occupied in the ground state; and the ratio 3:6:1 for Nb, Mo, Ru, Rh, and Ag, where the s is singly occupied in the ground state. For Pd, the average was taken of the d^{10}, $d^9 s$ and $d^8 p^2$ configurations in the ratio 6:3:1, and for Cd the average was taken of the $d^{10} s^2$ and $d^{10} p^2$ configurations in the ratio 3:1.

To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed on Zr and Cd, 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 4d/5s correlation in the tz basis sets, the correlating set was 2s2p2d2f1g. The large and small component coefficients of these correlating functions were determined by diagonalizing the Fock matrix in the space of the DHF occupied functions plus the primitive functions, and orthogonalizing the resultant extra functions to the DHF occupied functions.

The selection of primitives that gave the lowest energy was chosen, in most cases, to determine the contraction pattern. Where there was a difference between the calculations for Cd and for Zr, a compromise that gave the smallest error for either element was chosen. This procedure was used for 4d5s correlation and for 4s4p correlation. For 4s4p correlation there is significant overlap of the tz and qz correlating functions with the valence correlating functions. This is not surprising because the relativistic expansion of the 4d shell and contraction of the 4s and 4p shells is small.

3 Primitive basis sets

The SCF basis set sizes for the 5p block are 21s15p10d for dz, 28s21p14d for tz, and 33s27p17d for qz. For the 4d block, it was found that the same number of s functions could be used, but the number of p and d functions had to be reduced to maintain the correct number of

Table 1 Configuration average total Dirac–Hartree–Fock energies in E_h for uncontracted basis set calculations on the ground configurations

Element	Double-zeta	Triple-zeta	Quadruple-zeta	Numeric
Y	−3383.749444	−3383.761481	−3383.761805	−3383.763129
Zr	−3597.069855	−3597.082965	−3597.083318	−3597.083337
Nb	−3818.132530	−3818.148156	−3818.148593	−3818.148615
Mo	−4047.124173	−4047.141067	−4047.141533	−4047.141557
Tc	−4284.096005	−4284.112895	−4284.113345	−4284.113368
Ru	−4529.249433	−4529.269144	−4529.269684	−4529.269710
Rh	−4782.624398	−4782.645676	−4782.646259	−4782.646287
Pd	−5044.375437	−5044.400341	−5044.401061	−5044.401093
Ag	−5314.608796	−5314.633577	−5314.634257	−5314.634289
Cd	−5593.292962	−5593.318129	−5593.318807	−5593.318837

Table 2 Configuration average total Dirac–Hartree–Fock energies in E_h for uncontracted basis set calculations on the weighted average of configurations used for the basis set contractions

Element	Double-zeta	Triple-zeta	Quadruple-zeta
Y	−3383.702155	−3383.715818	−3383.716310
Zr	−3597.033816	−3597.048279	−3597.048744
Nb	−3818.129477	−3818.145046	−3818.145481
Mo	−4047.120095	−4047.136901	−4047.137364
Tc	−4284.099678	−4284.117768	−4284.118293
Ru	−4529.212734	−4529.232171	−4529.232703
Rh	−4782.573294	−4782.594291	−4782.594865
Pd	−5044.255595	−5044.279898	−5044.280596
Ag	−5314.507058	−5314.531533	−5314.532204
Cd	−5593.262493	−5593.287706	−5593.288384

Table 3 Exponents of valence 4d correlating and diffuse f functions and 3d correlating f function for the double-zeta basis sets

Element	4d correlating f	4d diffuse f	3d correlating f
Y	3.43324E−01	9.88718E−02	9.70596E+00
Zr	4.72998E−01	1.28998E−01	1.05908E+01
Nb	5.49722E−01	1.18902E−01	1.15101E+01
Mo	6.75480E−01	1.42226E−01	1.24615E+01
Tc	8.02895E−01	2.25819E−01	1.34457E+01
Ru	9.33446E−01	1.90509E−01	1.44648E+01
Rh	1.07042E+00	2.15635E−01	1.55167E+01
Pd	1.17180E+00	1.67287E−01	1.66108E+01
Ag	1.35676E+00	2.70460E−01	1.77308E+01
Cd	1.54575E+00	3.86147E−01	1.88860E+01

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

Element	f	f	g
Y	1.98129E−01	9.34357E−02	1.98466E−01
Zr	6.73952E−01	1.73883E−01	3.12817E−01
Nb	1.01821E+00	2.91833E−01	5.33556E−01
Mo	1.22377E+00	3.58162E−01	6.90567E−01
Tc	1.45235E+00	4.43195E−01	8.58696E−01
Ru	1.64060E+00	4.94623E−01	1.00671E+00
Rh	1.86029E+00	5.66866E−01	1.17513E+00
Pd	1.97981E+00	5.85291E−01	1.33003E+00
Ag	2.37680E+00	7.58521E−01	1.62876E+00
Cd	2.62069E+00	8.39674E−01	1.78753E+00

Table 5 Exponents of diffuse 1f1g functions for the triple-zeta basis sets

Element	f	g
Y	3.11452E−02	6.61553E−02
Zr	5.79610E−02	1.04273E−01
Nb	9.72777E−02	1.77852E−01
Mo	1.19387E−01	2.30189E−01
Tc	1.47732E−01	2.86232E−01
Ru	1.64874E−01	3.35569E−01
Rh	1.88955E−01	3.91711E−01
Pd	1.95097E−01	4.43342E−01
Ag	2.52840E−01	5.42919E−01
Cd	2.79891E−01	5.95845E−01

Table 6 Exponents of 3d correlating 2f1g functions for the triple-zeta basis sets

Element	f	f	g
Y	1.85359E+01	5.83038E+00	1.18725E+01
Zr	2.01881E+01	6.40037E+00	1.29561E+01
Nb	2.19031E+01	6.99390E+00	1.40819E+01
Mo	2.36733E+01	7.60731E+00	1.52473E+01
Tc	2.55000E+01	8.24099E+00	1.64527E+01
Ru	2.73926E+01	8.89943E+00	1.77012E+01
Rh	2.93422E+01	9.57826E+00	1.89899E+01
Pd	3.13738E+01	1.02888E+01	2.03313E+01
Ag	3.34446E+01	1.10117E+01	2.17033E+01
Cd	3.55787E+01	1.17576E+01	2.31185E+01

functions per antinode across the block. Thus, the base p sets (for the 2p–4p functions) were 12p, 17p, and 21p for the dz, tz, and qz sets. With the addition of functions for the 5p shell, the final p sets were 14p, 20p, and 25p. It was found necessary to remove one d function from the tz set. The final basis set sizes including the 5p were therefore 21s14p10d for dz, 28s20p13d for tz, and 33s25p17d for qz.

Configuration average total DHF energies for the ground configuration from calculations using these

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

Element	f	f	f	g	g	h
Y	2.39159E−01	2.07282E−01	8.28418E−02	3.25387E−01	1.25835E−01	2.36519E−01
Zr	1.02399E+00	3.36807E−01	1.25481E−01	6.44824E−01	2.01300E−01	3.46937E−01
Nb	1.52701E+00	5.37431E−01	1.91072E−01	9.51411E−01	2.88657E−01	6.24396E−01
Mo	1.81106E+00	6.52516E−01	2.33728E−01	1.17047E+00	3.68264E−01	8.19423E−01
Tc	1.91277E+00	6.81936E−01	2.36464E−01	1.35722E+00	4.35280E−01	9.45784E−01
Ru	2.39042E+00	8.90437E−01	3.23511E−01	1.61790E+00	5.41753E−01	1.18648E+00
Rh	2.72353E+00	1.02594E+00	3.73890E−01	1.85263E+00	6.38121E−01	1.36747E+00
Pd	2.86610E+00	1.06564E+00	3.72280E−01	2.04666E+00	7.13685E−01	1.51283E+00
Ag	3.33094E+00	1.27994E+00	4.71950E−01	2.35526E+00	8.62427E−01	1.73566E+00
Cd	3.63132E+00	1.40791E+00	5.29555E−01	2.63745E+00	9.95665E−01	1.95265E+00

Table 8 Exponents of diffuse 1f1g1h functions for the quadruple-zeta basis sets

Element	f	g	h
Y	2.76139E−02	4.19451E−02	7.88398E−02
Zr	4.18270E−02	6.71001E−02	1.15646E−01
Nb	6.36907E−02	9.62191E−02	2.08132E−01
Mo	7.79093E−02	1.22755E−01	2.73141E−01
Tc	7.88214E−02	1.45093E−01	3.15261E−01
Ru	1.07837E−01	1.80584E−01	3.95495E−01
Rh	1.24630E−01	2.12707E−01	4.55824E−01
Pd	1.24093E−01	2.37895E−01	5.04278E−01
Ag	1.57317E−01	2.87476E−01	5.78552E−01
Cd	1.76518E−01	3.31889E−01	6.50882E−01

Table 9 Exponents of 2f1g functions for 4s4p correlation for the quadruple-zeta basis sets

Element	f	f	g
Y	1.45868E+00	7.13780E−01	1.29800E+00
Zr	1.63286E+00	8.08557E−01	1.46379E+00
Nb	1.81206E+00	8.92544E−01	1.60147E+00
Mo	2.00075E+00	9.89849E−01	1.76798E+00
Tc	2.17580E+00	1.09289E+00	1.97015E+00
Ru	2.36497E+00	1.17685E+00	2.11748E+00
Rh	2.56798E+00	1.27931E+00	2.29534E+00
Pd	2.76906E+00	1.36589E+00	2.45874E+00
Ag	2.97036E+00	1.48023E+00	2.67382E+00
Cd	3.19038E+00	1.60400E+00	2.90159E+00

basis sets, uncontracted, are compared with the numerical values in Table 1.

Configuration average total DHF energies from calculations using the uncontracted SCF basis sets for the average of the $d^{n+1}s^1$, d^ns^2, and d^np^2 configurations, weighted according to the procedure described above, are given in Table 2. The calculations that generated these energies were used to provide DHF contraction coefficients. These energies are provided as reference energies for the contracted basis sets.

The valence correlating functions, diffuse functions, and 3d core correlating functions for the double-zeta basis sets are presented in Table 3. The valence correlating functions, diffuse functions, and 3d core correlating functions for the triple-zeta basis sets are presented in Tables 4, 5, and 6. The valence correlating functions, diffuse functions, 2f1g function for 4s4p correlation, and 3d core correlating functions for the quadruple-zeta basis sets are presented in Tables 7, 8, 9, and 10.

For the tz basis sets, the f exponent for 4s4p correlation is close to the inner f exponent for 4d5s correlation except at the beginning of the block, where the valence correlating functions are much more diffuse. By Nb, the ratio between these two exponents is less than 1.4, and

including the 4s4p correlating function in the basis set is likely to result in linear dependence.

In the qz basis set, there is a near linear dependence in the f set for 4d5s correlation in Y: the ratio of the inner two exponents is less than 1.2. Starting the optimization with a variety of exponents gave the same result. However, the surface is quite flat, so the optimization does not lead to much change in the energy. As for the tz basis set, there is overlap between the sets for 4s4p correlation and 4d5s correlation. For Y, both f functions are needed for 4s4p correlation; for Zr only the tighter function is needed, and for the remainder, the 4d5s correlating set covers the 4s4p f space. The g function for 4s4p correlation is needed until Tc; after that the g space for 4d5s correlation covers this space well enough. This leads to a somewhat inconsistent set across the row, but the change is forced by the changing nature of the shells involved.

4 Contraction patterns

The MR-SDCI calculations that were performed to determine which functions to uncontract yielded the contraction patterns described below. The contracted

Table 10 Exponents of 3d correlating 3f2g1h functions for the quadruple-zeta basis sets

Element	f	f	f	g	g	h
Y	2.99053E+01	1.09352E+01	4.18367E+00	2.09549E+01	7.47091E+00	1.37185E+01
Zr	3.25444E+01	1.19650E+01	4.61522E+00	2.28307E+01	8.20006E+00	1.49767E+01
Nb	3.52802E+01	1.30342E+01	5.06485E+00	2.47784E+01	8.95930E+00	1.62839E+01
Mo	3.81006E+01	1.41376E+01	5.52887E+00	2.67906E+01	9.74444E+00	1.76369E+01
Tc	4.10085E+01	1.52764E+01	6.00782E+00	2.88686E+01	1.05560E+01	1.90361E+01
Ru	4.40186E+01	1.64564E+01	6.50591E+00	3.10213E+01	1.13991E+01	2.04856E+01
Rh	4.71174E+01	1.76722E+01	7.01904E+00	3.32405E+01	1.22687E+01	2.19816E+01
Pd	5.03547E+01	1.89460E+01	7.56047E+00	3.55527E+01	1.31790E+01	2.35394E+01
Ag	5.36413E+01	2.02368E+01	8.10660E+00	3.79104E+01	1.41052E+01	2.51320E+01
Cd	5.70365E+01	2.15731E+01	8.67190E+00	4.03439E+01	1.50618E+01	2.67751E+01

basis sets are formed by adding primitive functions to the SCF occupied spinor or orbital set. Two primary contraction patterns are described, for a valence basis set, which correlates the 5d and 6s orbitals; a valence + outer core set which adds functions for 5s and 5p correlation to the valence set. To any of these contractions, the relevant diffuse functions listed in Tables 3, 5, and 8 can be added. Extra diffuse functions are not needed for the s, p, and d sets.

The contraction patterns include an extra d function – the outermost – in the valence space, because flexibility of the d orbital is critical in transition metal complexes. However, if linear dependence is encountered in the d space, the outermost d function should not be uncontracted. The SCF set includes the 5p function, although 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 2nd s and p primtives, the 1st and 2nd d primitives, and the valence correlating f function (HF + 1s1p2d1f valence).
- *Valence + outer core:* to the valence set, add the 4th s primitive, the 3rd p primitive and the 3rd d primitive (HF + 1s1p2d1f valence + 1s1p1d outer core).

4.2 Triple-zeta basis sets

- *Valence:* to the SCF functions, add the 1st and 3rd s primitives, the 2nd and 3rd p primitives, the 1st through 3rd d primitives, and the valence correlating 2f1g functions (HF + 2s2p3d2f1g valence).

Table 11 Energies in eV of the $4d^9 5s^2$ states of Ag relative to the ground state $4d^{10} 5s^1$, from valence SDCI calculations as a function of basis set and spinors used

State	Basis set	$4d^9 5s^2$ spinors	$4d^{10} 5s^1$ spinors	Average spinors	Relaxed spinors
Exclucing outermost d					
$^2D_{5/2}$	dz	2.991	4.698	3.813	3.496
	tz	3.580	4.588	4.043	3.883
	qz	3.704	4.619	4.123	4.007
$^2D_{3/2}$	dz	3.551	5.308	4.396	4.055
	tz	4.136	5.170	4.611	4.439
	qz	4.260	5.195	4.689	4.563
SO-splitting	dz	0.560	0.611	0.582	
	tz	0.556	0.582	0.568	
	qz	0.556	0.577	0.566	
Inclucing outermost d					
$^2D_{5/2}$	dz	3.632	4.405	3.993	3.932
	tz	3.666	4.536	4.070	3.980
	qz	3.709	4.612	4.124	4.002
$^2D_{3/2}$	dz	4.186	4.975	4.556	4.487
	tz	4.221	5.110	4.635	4.536
	qz	4.265	5.188	4.690	4.558
SO-splitting	dz	0.555	0.571	0.563	
	tz	0.555	0.574	0.565	
	qz	0.556	0.576	0.566	

- *Valence + outer core:* to the valence set, add the 4th and 6th s primitives, the 5th and 6th and p primitives, the 4th and 5th d primitives, and the 4s4p correlating f function for Y and Zr (HF + 2s2p3d2f1g valence + 2s2p2d(1f) outer core).

4.3 Quadruple-zeta basis sets

- *Valence:* to the SCF functions, add the 1st, 2nd, and 4th s primitives, the 2nd through 4th p primitives, the 1st through 4th d primitives, and the valence correlating 3f2g1h set (HF + 3s3p4d3f2g1h valence).
- *Valence + outer core:* to the valence set add the 5th, 6th, and 8th s and p primitives, the 5th, 6th, and 7th d primitives, the 2f outer core primitives for Y, the

Table 12 Energies in eV of the $4d^95s^2$ states of Ag relative to the ground state $4d^{10}5s^1$, from SDCI calculations as a function of basis set, correlation level and spinors used

State	Basis set	Correlation level	$4d^95s^2$ spinors	$4d^{10}5s^1$ spinors	Average spinors	Relaxed spinors
$^2D_{5/2}$	dz	val	3.053	4.457	3.739	3.557
		+cv	2.873	4.165	3.490	3.249
		+cc	2.896	4.260	3.544	3.291
	tz	val	3.531	4.509	3.983	3.898
		+cv	3.363	4.412	3.836	3.759
		+cc	3.363	4.503	3.878	3.812
$^2D_{3/2}$	dz	val	3.614	5.051	4.316	4.117
		+cv	3.448	4.768	4.078	3.824
		+cc	3.472	4.866	4.135	3.868
	tz	val	4.088	5.087	4.551	4.455
		+cv	3.932	5.002	4.416	4.329
		+cc	3.934	5.097	4.459	4.383
SO-splitting	dz	val	0.561	0.595	0.577	
		+cv	0.575	0.603	0.588	
		+cc	0.577	0.606	0.591	
	tz	val	0.557	0.578	0.567	
		+cv	0.570	0.590	0.579	
		+cc	0.571	0.594	0.582	

val SDCI from 4d and 5s spinors, *+cv* add singles from 4s4p and simultaneous singles from 4s4p and 4d5s, *+cc* add doubles from 4s4p

2nd outer core primitive for Zr, and the outer core g primitives for Y–Rh (HF + 3s4p4d3f2g1h valence + 3s3p3d2f1g outer core; d and f sets overlap).

5 Application

One of the important issues in transition metal chemistry is the relaxation arising from d–s excitations [32]. The orbitals (or spinors) generated from the various d and s occupancies can be quite different, and it is necessary to overcome the orbital bias to obtain accurate energies, such as in complexes in which the s and d occupations change during a reaction. When using contracted basis sets, the issue of which orbital set to use for the contraction is critical.

To illustrate and investigate this issue, the primitive basis sets described above have been used for calculations on the $4d^{10}5s$ and $4d^95s^2$ configurations of the Ag atom. SCF calculations were performed with the primitive dz, tz, and qz basis sets for both configurations and for the average in which the two configurations are equally weighted. SDCI calculations were then performed on the three states arising from these two configurations: the ground $4d^{10}5s$ $^2S_{1/2}$ state and the $4d^95s^2$ $^2D_{5/2}$ and $^2D_{3/2}$ states. Three sets of CI calculations were performed, using spinors from each of the three SCF calculations. With these three calculations, the effect of the choice of orbital set for the contraction and the number

Table 13 Energies in eV of the $4d^95s^2$ states of Ag relative to the ground state $4d^{10}5s^1$, from valence CI calculations in the dz basis set as a function of excitation level and spinors used

State	Excitation level	$4d^95s^2$ spinors	$4d^{10}5s^1$ spinors	Average spinors	Relaxed spinors
$^2D_{5/2}$	SD	2.991	4.698	3.813	3.496
	SDT	3.575	3.999	3.792	3.662
$^2D_{3/2}$	SD	3.551	5.308	4.396	4.055
	SDT	4.128	4.572	4.355	4.215
SO-splitting	SD	0.560	0.611	0.582	
	SDT	0.553	0.573	0.563	

of uncontracted functions can be examined. The results presented also include the relaxed excitation energies.

In Table 11, results are presented in which the effect of increasing the basis set size in valence SDCI calculations is examined. The calculations were performed with and without the outermost d function. As can be expected, adding this function had the largest effect on the dz basis set, and the effect on the qz basis set is minor (less than 0.01 eV). The largest differences on going from tz to qz are around 0.1 eV. While this is by no means converged, it should be a reasonable starting point for extrapolation [33–35]. It is notable that increasing the basis set size does little for the orbital bias. The results obtained from the average configuration are the closest to the relaxed results in all cases. For the spin–orbit splitting, the relaxed results are those from the $4d^95s^2$ configuration.

Table 12 shows results from the correlation of the 4s and 4p shells. These calculations were performed without the outermost d function. The correlating orbital space (the external space in the CI calculation) includes functions for both 4d5s correlation and 4s4p correlation. The results labeled val therefore differ from those in Table 11 because of the expansion of the correlating space. Correlating the 4s and 4p shells has a modest effect on the excitation energies, and substantially improves the orbital bias for the dz basis set but does not remove it entirely.

Table 13 presents results in which the level of excitation was extended, in CI calculations in the dz basis set without the outermost d. Clearly, triple excitations substantially reduce the orbital bias, from more than 1.5 eV to less than 0.5 eV. In these calculations, the results from the $4d^9 5s^2$ spinors are now closer to the relaxed results than those from the average spinors.

The conclusion from this study is that triple excitations are required to overcome the orbital bias: neither basis set size nor core correlation are sufficient, if the level of excitation is restricted to singles and doubles. If this is not possible, use of averaged spinors provides the closest approximation to the relaxed results.

6 Internet archive

The full tables of basis sets including spin-free relativistic SCF [36] and Dirac–Fock SCF coefficients are available in ASCII format as an internet archive and also from the Dirac web site, http://dirac.chem.sdu.dk. The archive contains the Dirac–Fock SCF coefficients and the spin-free relativistic SCF coefficients, including the Foldy–Wouthuysen transformed large component coefficients, and the correlating and polarizing functions. Prescriptions are given for the construction of various basis sets.

References

1. Malli GL, Da Silva ABF, Ishikawa Y (1993) Phys Rev A 47:143
2. Malli GL, Da Silva ABF, Ishikawa Y (1994) J Chem Phys 101:6829
3. Fægri K Jr (2001) Theor Chem Acc 105:252
4. Fægri K Jr (2001) Chem Phys 311:25
5. Dyall KG (1998) Theor Chem Acc 99:366
6. Dyall KG (2002) Theor Chem Acc 108:365
7. Dyall KG (2002) Theor Chem Acc 108:335
8. Dyall KG (2006) Theor Chem Acc 115:441
9. Dyall KG (2004) Theor Chem Acc 112:403
10. Dyall KG (2006) Theor Chem Acc (in press)
11. Koga T, Tatewaki H, Matsuoka O (2001) J Chem Phys 115:3561
12. Koga T, Tatewaki H, Matsuoka O (2002) J Chem Phys 117:7813
13. Koga T, Tatewaki H, Matsuoka O (2003) J Chem Phys 119:1279
14. Tatewaki H, Watanabe Y (2004) J Chem Phys 121:4528
15. Douglas M, Kroll NM (1974) Ann Phys (NY) 82:89
16. Hess BA (1985) Phys Rev A 32:756
17. Hess BA (1986) Phys Rev A 33:3742
18. Tsuchiya T, Abe M, Nakajima T, Hirao K (2001) J Chem Phys 115:4463
19. Nakajima T, Hirao K (2002) J Chem Phys 116:8270
20. Osanai Y, Noro T, Miyoshi E (2002) J Chem Phys 117:9623
21. Noro T, Sekiya M, Osanai Y, Miyoshi E, Koga T (2003) J Chem Phys 119:5142
22. Osanai Y, Noro T, Miyoshi E, Sekiya M, Koga T (2004) J Chem Phys 120:6408
23. Balabanov NB, Peterson KA (2005) J Chem Phys 123:064107
24. Peterson KA, Puzzarini C (2005) Theor Chem Acc 114:283
25. Dunning TH Jr (1989) J Chem Phys 90:1007
26. Kendall RA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96:6769
27. Woon DE, Dunning TH Jr (1993) J Chem Phys 98:1358
28. Wilson AK, Woon DE, Peterson KA, Dunning TH Jr (1999) J Chem Phys 110:7667
29. Dyall KG, Fægri K Jr (1996) Theor Chim Acta 94:39
30. Seth M, Shepard R, Wagner A, Dyall KG (2001) J Phys B 34:2383
31. Visscher L, Dyall KG (1997) At Data Nucl Data Tables 67:207
32. Bauschlicher CW, Langhoff SR, Partridge H. In: Yarkony DR (ed) Modern electronic structure theory, Part II. World Scientific, Singapore, p 1280
33. Feller D (1992) J Chem Phys 96:6104
34. Martin JML (1996) Chem Phys Lett 259:669
35. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
36. Dyall KG (1994) J Chem Phys 100:2118