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Systematically convergent basis sets for transition metals. II. Pseudopotential-based correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements

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Abstract Sequences of basis sets that systematically converge towards the complete basis set (CBS) limit have been developed for the coinage metals (Cu, Ag, Au) and group 12 elements (Zn, Cd, Hg). These basis sets are based on recently published small-core relativistic pseudopotentials [Figgen D, Rauhut G, Dolg M, Stoll H (2005) Chem Phys 311:227] and range in size from double- through quintuple- ζ . Series of basis sets designed for valence-only and outer-core electron correlation are presented, as well as these sets augmented by additional diffuse functions for the accurate description of negative ions and weak interactions. Selected benchmark calculations at the coupled cluster level of theory are presented for both atomic and molecular properties. The latter include the calculation of both spectroscopic and thermochemical properties of the homonuclear dimers Cu₂, Ag₂, and Au₂, as well as the van der Waals species Zn₂, Cd₂, and Hg₂. The CBS limit results, including the effects of core-valence correlation and spin-orbit coupling, represent some of the most accurate carried out to date and result in new recommendations for the equilibrium bond lengths of the group 12 dimers. Comparisons are also made to a limited number of all-electron Douglas–Kroll–Hess (DKH) calculations (second and third order) carried out using new correlation consistent basis sets of triple- ζ quality.

Keywords Basis sets · Correlation · Consistent · Transition metal dimers · Complete basis set · Coupled cluster

1 Introduction

With the advent of atomic natural orbital (ANO) [1] and correlation consistent (cc) [2] basis sets, errors due to basis set truncation effects in the solutions of the electronic Schrödinger equation could be addressed in a systematic manner. In the particular case of correlation consistent basis sets, various extrapolation formulas have been used that can provide accurate estimates of the complete basis set (CBS) limit for various atomic and molecular properties, thereby removing errors due to an incomplete basis. This then greatly facilitates the analysis of the errors *intrinsic* to the chosen wavefunction approximation, e.g., Møller–Plesset perturbation or coupled cluster theory. Having this kind of control over the errors in a calculation has proven to be essential in the area of ab initio thermochemistry [3–7], where removing basis set truncation errors is a necessary ingredient for reliably obtaining chemical accuracy (<1 kcal/mol). Until recently, however, correlation consistent basis sets have not been generally available for the transition metal elements or even main group elements heavier than krypton. In the case of the post-*d* elements Ga–Rn, correlation consistent basis sets based on accurate relativistic pseudopotentials were only recently developed [8, 9] and were shown to have convergence properties in molecular calculations similar to those now commonly observed for lighter elements. In regards to the transition metal elements, correlation consistent all-electron basis sets had been previously developed by Bauschlicher and coworkers for just two elements, Ti and Fe [10, 11]. Very recently, however, both nonrelativistic and scalar relativistic cc-type basis sets (all-electron) from triple- to quintuple- ζ have been reported for Sc–Zn [12].

While there are many basis set choices for the first row transition metal atoms (Ref. [12] and references therein), accurate basis sets for correlated calculations on the second and third row transition metals are more scarce. Except for the recent nonrelativistic basis sets of Osanai et al. [13] for Y–Cd and the relativistic basis sets of Dyall [14] for Hf–Hg, these are, with a few exceptions, limited to relatively small sets [15–17], including those accompanying relativistic effective

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core potentials (ECPs) [18–26]. Third-order Douglas–Kroll optimized basis sets have also recently been reported by Hirao and coworkers [27,28], but these sets are only between double- and triple- ζ quality.

While full families of accurate relativistic cc basis sets could certainly also be developed for the second and third row transition metals using, e.g., the Douglas–Kroll–Hess (DKH) Hamiltonian [29,30] for scalar relativity, the required sizes of the underlying Hartree–Fock (HF) primitive sets could become prohibitively large. On the other hand, small-core relativistic pseudopotentials (PPs) or effective core potentials (ECPs) are capable of accurately recovering both scalar and spin-orbit relativistic effects with the added benefit of removing the requirement for explicit basis functions describing the low-lying core electrons since these are removed by the pseudopotential. Just as the development of the PP-based post- d correlation consistent basis sets [8,9] were motivated by new, next-generation PPs by the Stuttgart/Köln groups [24,25], the present work was also initiated by the adjustment of new pseudopotentials for the group 11 and 12 elements by these same groups [26]. This paper reports the development of correlation consistent-type basis sets for Cu–Au and Zn–Hg based on the small core relativistic PPs of Figgen et al. [26]. The resulting sets are denoted cc-pV nZ -PP for valence-only correlation, cc-pwCV nZ -PP for valence plus outer-core correlation, and aug-cc-p(wC)V nZ for their diffuse function-augmented versions. In each case nZ ranges from DZ to 5Z and they are very similar in construction to the previously reported basis sets for both the first row transition metals (all-electron) and the post- d elements (PP-based). Some preliminary basis sets of this type had been previously reported [31] for the Hg atom using the older PP of Häussermann et al. [32], and the present work supercedes those sets.

Of course, it is still important to also determine what additional errors have been introduced into the calculations by using the PP approximation. To provide the best possible comparison, all-electron basis sets of triple- ζ quality have also been developed in this work for the second and third row transition metal elements of this study using the DKH Hamiltonian (cc-pVTZ-DK, cc-pwCVTZ-DK, and aug-cc-p(wC)VTZ-DK). The determination of basis sets for all the remaining elements of the transition metal series that are equivalent to the present work, both PP-based and all-electron, is also currently underway [33].

The details of the basis set development is described in Sect. 2.1, which is followed in Sect. 2.2 by a description of the atomic (excitation energies, electron affinities, ionization potentials) and molecular (spectroscopic and thermochemical properties of Cu₂, Ag₂, Au₂, Zn₂, Cd₂, Hg₂) benchmark calculations that have been carried out to ascertain the accuracy and efficiency of the new basis sets and underlying PPs. The results of the benchmark calculations are presented and discussed in Sect. 3 with conclusions given in Sect. 4.

2 Methodology

2.1 Basis set construction

The basis set development of the present work closely follows that of the all-electron correlation consistent basis sets for the first row transition metals that were recently developed in this laboratory [12] (cc-pV nZ -DK and cc-pV nZ with $n = T, Q,$ and 5). The present cases mainly differ by the use of small-core relativistic pseudopotentials that replace the inner core electrons, yielding basis set series denoted as cc-pV nZ -PP ($n = D, T, Q,$ and 5). Specifically the pseudopotentials correspond to the recently reported Stuttgart/Köln energy consistent PPs that were adjusted to all-electron four-component multi-configuration Dirac–Hartree–Fock (MCDHF) calculations, including the two-electron Breit interaction [26]. These PPs replace the $1s-2p$, $1s-3d$, and $1s-4f$ cores of Cu–Zn, Ag–Cd, and Au–Hg, respectively. As in our previous work, the exponents of the present basis sets were optimized employing double-sided numerical derivatives within a BFGS algorithm [34]. The energy gradients were typically converged to better than 1×10^{-6} . The MOLPRO program suite [35] was used throughout and only the pure spherical harmonic components of the $dfghi$ angular momentum functions were utilized. All orbitals were fully symmetry equivalenced and the frozen core approximation was imposed throughout unless otherwise noted.

Naturally the largest difference between the present PP-based basis sets and the all-electron ones is the decrease in the number of primitive spd functions required for the Hartree–Fock (HF) description of the atoms due to the removal of the low-lying core electrons from the calculations. As in the all-electron case, the choice of HF primitive set for a particular correlation consistent basis set is dictated both by the error in the atomic HF calculation relative to the HF limit and the qualitative nature of the outermost exponents, e.g., the set chosen for the cc-pVDZ-PP basis set should provide a double- ζ description of the ns valence orbital. The sizes chosen for the present work, which are shown in Table 1, were nearly identical to those employed previously for the post- d cc-pV nZ -PP basis sets [8,9] and smoothly converge the atomic HF energies to within a few μE_h of the apparent HF limits as the basis set is increased from DZ to 5Z. As in the all-electron transition metal basis sets, the HF s functions were fully optimized for the ns^2 states of the atoms, while the p exponents were obtained from calculations on the lowest $ns^2(n-1)d^8np^1$ and $ns^2(n-1)d^9np^1$ atomic states for the group 11 and 12 elements, respectively. The specific states used were the same as those given in Ref. [12] for Cu and Zn. The optimization of the HF d functions were also carried out in the same manner as the all-electron basis sets. Namely, the d exponents for the coinage metal atoms were determined in state-averaged HF calculations involving both the $ns^2(n-1)d^9$ and $ns^1(n-1)d^{10}$ states in order to obtain a sufficiently

Table 1 Composition of the basis sets (primitives)/[contracted], developed in the present work

Basis set		
cc-pVDZ-PP		(8s7p6d1f)/[4s4p3d1f]
cc-pVTZ-PP		(10s9p8d2f1g)/[5s5p4d2f1g]
cc-pVQZ-PP	(14s11p11d3f2g1h)/[6s6p5d3f2g1h] ^a	(14s11p10d3f2g1h)/[6s6p5d3f2g1h] ^b
cc-pV5Z-PP	(16s13p12d4f3g2h1i)/[7s7p6d4f3g2h1i] ^a	(16s13p11d4f3g2h1i)/[7s7p6d4f3g2h1i] ^b
cc-pwCVDZ-PP		[4s4p3d] + 1s1p1d2f
cc-pwCVTZ-PP		[5s5p4d] + 2s2p2d3f2g
cc-pwCVQZ-PP		[6s6p5d] + 2s2p2d4f3g2h
cc-pwCV5Z-PP		[7s7p6d] + 2s2p2d5f4g3h2i
aug-cc-pVDZ-PP		cc-pVDZ-PP + 1s1p1d1f
aug-cc-pVTZ-PP		c-pVTZ-PP + 1s1p1d1f1g
aug-cc-pVQZ-PP		cc-pVQZ-PP + 1s1p1d1f1g1h
aug-cc-pV5Z-PP		cc-pV5Z-PP + 1s1p1d1f1g1h1i
cc-pVTZ-DK	(20s16p8d2f1g)/[7s6p4d2f1g] ^c	(26s21p14d2f1g)/[8s7p5d2f1g] ^d (32s28p19d13f1g)/[9s8p6d3f1g] ^e
cc-pVQZ-DK	(22s18p10d3f2g1h)/[8s7p5d3f2g1h] ^c	(32s25p18d3f2g1h)/[9s8p6d3f2g1h] ^f

^a Cu/Zn^b Ag/Cd, Au/Hg^c Ref. [12]^d Ag/Cd^e Au/Hg^f Determined for Cd only

diffuse set of d exponents. The analogous exponents for the group 12 elements were only optimized for the ground $ns^2(n-1)d^{10}$ configuration. The resulting spd HF primitive sets were then generally contracted to $[2s1p1d]$ using atomic orbital (AO) coefficients from either state-averaged (s^2 and s^1 , group 11) or single-state (s^2 , group 12) HF calculations. An additional contracted p function was also included to describe the valence np atomic orbital. These contraction coefficients were obtained from HF calculations on the same states described above for the p exponent optimizations.

The correlating functions that were added to the contracted $[2s2p1d]$ basis sets also followed the same general prescription as the all-electron transition metal sets [12]. The spd correlating functions were obtained from state-averaged (2 states for group 11, 1 state for group 12) configuration interaction singles and doubles (CISD) atomic natural orbitals (ANOs); $1s1p1d$ for DZ, $2s2p2d$ for TZ, $3s3p3d$ for QZ, and $4s4p4d$ for 5Z. Using ANOs rather than simply uncontracting functions from the HF sets avoids the special problems associated with pseudopotential basis sets as outlined previously by Blaudeau et al. [36] and Christiansen [37]. In order to provide additional flexibility, the outermost exponent was also uncontracted from the HF set. The number and type of higher angular momentum functions follows the expected pattern, i.e., $1f$ for DZ, $2f1g$ for TZ, $3f2g1h$ for QZ, and $4f3g2h1i$ for 5Z. These exponents were constrained to have an even tempered distribution [38,39], i.e., $\zeta_k = \alpha\beta^k$, and were optimized for the CISD energy of either a two-state average (group 11) or the ground-state (group 12). It might be noted that the resulting $2f1g$ exponents for the cc-pVTZ-PP basis sets were very similar to those optimized previously by Martin and Sundermann [40] using quasirelativistic Stuttgart-type pseudopotentials [23,41].

Recovering the effects of core-valence electron correlation generally requires the addition of extra correlating functions, and cc-pwCVnZ-PP basis sets ($n = D, T, Q, 5$) have been

developed in this work following the same procedure as the all-electron sets [12]. The additional functions were designed for correlating the outer-core $(n-1)sp$ electrons and the weighted core-valence prescription [42] was followed, i.e., the exponents were optimized for the intershell, core-valence CISD correlation energy with the addition of just 1% of the total intrashell, core-core correlation energy (s^2 state only in each case). To each cc-pVnZ-PP basis set with $n = T, Q$, and 5, a set of uncontracted $2s2p2d$ functions optimized in this manner was added. Only a $1s1p1d$ set of core-valence functions was added to the DZ basis set. As in the all-electron basis sets [12], the higher angular momentum functions ($fghi$) were determined by retaining only the most diffuse functions from the cc-pVnZ-PP basis sets and optimizing even tempered sequences of functions for the sum of the weighted core-valence correlation energy and the valence correlated CISD energy (state averaged energy for group 11). The final composition of the resulting cc-pwCVnZ-PP basis sets are shown in Table 1.

Finally, in order to accurately describe negative ions and weakly bound systems, diffuse augmented basis sets were developed. As in the all-electron transition metal work, these additional functions, one in each angular momentum symmetry, were simply obtained as even tempered extensions of the outermost functions in the cc-pwCVnZ basis sets. These exponents are then added to the cc-pVnZ-PP and cc-pwCVnZ-PP basis sets to obtain aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP basis sets, respectively.

To complement the all-electron DK relativistic basis sets previously developed for the first row transition metals, similar basis sets at the TZ level have also been developed for both the second and third row elements of this work in order to provide unambiguous comparisons with the PP-based basis set results. In the case of Cd, a QZ quality basis set was also optimized. The only differences between the construction of the all-electron sets and the PP basis sets outlined above was

in the larger sizes of the underlying HF primitive sets and the use of the one-electron (second-order) DKH Hamiltonian for the treatment of scalar relativity. In the case of Ag and Cd, the *spd* primitive sets optimized for the cc-pVTZ-DK basis sets corresponded to (26s21p14d), while the cc-pVQZ-DK basis for Cd consisted of (32s25p18d). The HF primitive sets for Au and Hg consisted of (32s28p19d11f) for cc-pVTZ-DK. These choices of primitive sets resulted in outermost exponents very similar to the PP basis sets. The same electronic states were used in the exponent optimizations as detailed above, but the Legendre expansion method of Petersson et al. [43] was utilized for most of the exponents instead of carrying out full optimizations. Specifically, for each angular momentum symmetry a six-term Legendre expansion was used for the innermost functions while the outermost five exponents were fully optimized. This is the same method as was used previously for the cc-pV5Z-DK basis sets for the first row transition metal elements [12], and initial tests on Cd in nonrelativistic calculations yielded an optimized (26s) set of exponents very similar to the fully optimized set of Partridge and Faegri [44]. The present procedure differed only in the case of the 11f set for Au and Hg, where just the six-term Legendre expansion was used. Lastly, in each case final valence-only cc-pVnZ-DK, core-valence cc-pwCVnZ-DK, and diffuse augmented aug-cc-pVnZ-DK (and aug-cc-pwCVnZ-DK) basis sets ($n = T$ for all, $n = Q$ also for Cd) were constructed from these primitive sets in an identical manner as the PP-based sets. Their final compositions (cc-pVnZ-DK only, the others are analogous to the PP-based ones) are shown in Table 1.

2.2 Benchmark calculations

The efficacy of the basis sets of the present work have been evaluated in both atomic and molecular benchmark calculations at the coupled cluster singles and doubles with perturbative triples [CCSD(T)] level of theory [45, 46]. Both valence only and valence plus outer-core electron correlation calculations have been carried out. In the case of the atomic calculations, the properties considered were the electron affinities and $s^1d^{10} \rightarrow s^2d^9$ excitation energies for the coinage metals, as well as the ionization potentials of all six elements of the present work. The open-shell atomic calculations utilized the R/UCCSD(T) variant [47–50], i.e., restricted open-shell HF (ROHF) orbitals were employed but some spin contamination is allowed in the solution of the CCSD equations. Molecular benchmark calculations on the strongly bound coinage metal dimers (Cu_2 , Ag_2 , Au_2) involved computing 7–9 points on their near-equilibrium potential energy curves, fitting the resulting energies to sixth order polynomials in bond displacement coordinates, and carrying out the usual Dunham analysis [57] to determine equilibrium bond lengths, harmonic frequencies, anharmonicities, and dissociation energies. The group 12 van der Waals dimers were treated in a similar manner, except that the function counterpoise (CP) correction [52] was included.

Also in these latter cases, in addition to the standard diffuse augmented basis sets doubly-augmented sets [53] (d-aug-cc-pVnZ) were also employed, where the additional diffuse functions (one for each angular momentum symmetry) were obtained by simply scaling the outermost exponents of the aug-cc-pVnZ sets (PP and DK) by a factor of 0.40.

To thoroughly test the accuracy of the underlying pseudo-potentials in the molecular calculations, spin-orbit (SO) calculations were also carried out for each of the molecules of this study. These SO calculations employed the aug-cc-pVTZ-PP basis sets in each case and utilized the SO parameters that accompany the PPs [26]. At each point on the diatomic potential energy curves, a SO correction to the energy was obtained as the difference between the energy obtained in a CI calculation without the SO interaction and one with it included. These calculations were carried out with the COLUMBUS program [54], and the SO CI calculations utilized the double-group SO-CI program of Pitzer and coworkers [55], where in the present cases all possible singlet and triplet states were mixed via the SO operator. The SO-CI calculations on the coinage metal dimers were carried out at the multireference configuration interaction (MRCISD) level of theory using a complete active space self-consistent field reference space, but with only the two valence *s* electrons active. The group 12 dimers were treated at the single reference CISD level of theory. In all cases, only the valence electrons were correlated and the dissociation limits were calculated in the supermolecule approximation with a bond length of 50 bohr.

Finally, in the all-electron calibration calculations employing the cc-pVnZ-DK basis sets, the accuracy of the second-order DKH Hamiltonian was also investigated by carrying out a limited number of calculations employing both the DK2 and DK3 Hamiltonians [56–58] as implemented in the UTChem program [59]. These calculations were performed at each point on the potential energy curves using second order Møller-Plesset perturbation theory (MP2, valence correlation only), the aug-cc-pVTZ-DK basis sets, and with unrestricted HF orbitals for the open-shell species. The differences in the two energies (DK2 and DK3) were then added to the DK-CCSD(T) potential energy curves determined using MOLPRO for a subsequent spectroscopic constant analysis. Analogous calculations were also carried out in relation to the atomic electron affinities and ionization potentials.

It should also be noted that in the all-electron (DK2) core-valence calculations on Au_2 and Hg_2 , the 5s electrons were correlated together with the 5p electrons in order to be consistent with the PP-based work. This is problematic for these species since the Au and Hg relativistic 4f orbitals lie higher in energy than the 5s. (Note, in the atomic calculations these orbitals appear in different symmetries and hence do not present any special problems.) In the present work, the two 5s-type orbitals were simply rotated above the core 4f-type orbitals prior to the CCSD(T) calculations.

The fundamental advantage in using a sequence of basis sets that exhibit systematic, regular convergence towards the CBS limit is the possibility of extrapolating the results

accurately and thereby removing basis set truncation errors. As in previous work, we have generally utilized two extrapolation formulas [60–62],

$$E_n = E_{\text{CBS}} + An^{-3} \quad (1)$$

$$E_n = E_{\text{CBS}} + Ae^{-(n-1)} + Be^{-(n-1)^2} \quad (2)$$

where n is the cardinal number of the basis set ($n = 2$ for DZ, $n = 3$ for TZ, etc.) and E_{CBS} is the resulting estimate of the CBS limit. Past experience has indicated that with basis sets of the sizes used in the present work, Eq. (1) sometimes tends to slightly overestimate the true CBS limit while Eq. (2) generally provides an underestimate. Hence the average value obtained from these two expressions has been used in the past as a conservative estimate of the actual CBS limit [5, 12, 63]. In the present work, two-point extrapolations using Eq. (1) with QZ and 5Z basis sets have been used throughout on only the CCSD(T) correlation energies. The HF energies were not extrapolated in these cases and the 5Z HF values were simply taken as the most accurate estimates of the HF limits. In the cases of the group 12 van der Waals dimers, the CP corrected HF and correlation energy contributions to the binding energies were used. Extrapolations using Eq. (2) were carried out only for the group 12 dimers, which showed much slower basis set convergence with the aug-cc-pVnZ-PP basis sets (and hence more susceptible to overshooting by Eq. (1)). In these cases a three-point extrapolation was carried out on the total energies with Eq. (2) using basis sets from TZ to 5Z. The CBS limits cited for the van der Waals species correspond to the average of the values resulting from Eqs. (1) and (2).

3 Results and discussion

3.1 Atomic properties

CCSD(T) results as a function of basis set are shown in Tables 2, 3, and 4 for the atomic excitation energies, electron affinities, and ionization potentials, respectively. Smooth convergence with respect to the VnZ-PP basis sets is observed in all cases. Focusing first on the $s^1d^{10} \rightarrow s^2d^9$ excitation energies of the coinage metals shown in Table 2, the valence electron correlated results all converge from below the apparent CBS limit as the basis set is increased in size. As noted in the previous all-electron work for the late transition metals [12], the diffuse augmented basis set series yields a more rapid convergence towards the CBS limit. Tests on the Cu atom indicate that more than half of this improvement is due to the diffuse f -type functions in the aug-cc-pVnZ-PP basis sets, which points to the importance of sd correlation effects for this property. This effect appears to be less important down the series Cu, Ag, Au. It should also be noted, however, that nearly identical extrapolated CBS limits are obtained for these excitation energies when either the cc-pVnZ-PP or aug-cc-pVnZ-PP basis set series are utilized. The effects of correlating the $(n - 1)$ sp electrons are also shown in Table 2 using the (aug-)cc-pwCVnZ-PP basis sets. In each case

core-valence correlation decreases the state separation, particularly in the cases of Ag and Au where the excitation energy is decreased by 5–6 kcal/mol at the CBS limit. The effect for Cu is nearly zero at the CBS limit. On comparison to all-electron DK results using aug-cc-pwCVTZ-DK basis sets, it is evident that the PP approximation overestimates the overall effects of core-valence correlation (i.e., the s^2d^9 state is over-stabilized) by about 1–1.5 kcal/mol for this particular property. This is also exhibited in the final comparisons between theory and experiment in Table 2, where the CCSD(T) values are consistently too small by 0.6–2.1 kcal/mol. Accounting for PP errors of the magnitude noted above brings all three to within chemical accuracy.

These excitation energies were also calculated at the CCSD(T) level by Figgen et al [26] in the course of evaluating their PP adjustments. Their basis sets were similar to the present aug-cc-pVTZ-PP sets, however, they were used completely uncontracted. On their own these results appeared to be relatively far from experiment, but most of these errors can now clearly be attributed to the use of a finite basis set and not to inaccuracies in the pseudopotentials.

The calculated electron affinities for the coinage metal elements shown in Table 3 exhibit excellent convergence with respect to basis set (aug-series), both for valence-only correlated and in the core-valence calculations. In fact the aug-cc-pVTZ-PP results are within 1.5 kcal/mol of the CBS limits. In the case of the electron affinities, the differences between the PP-based calculations and the all-electron DK ones are much smaller than observed for the excitation energies, generally only a few tenths of a kcal/mol even for the core-valence correlation effects. The latter values are again appreciable in the cases of Ag and Au where $(n - 1)$ sp correlation is calculated to increase the electron affinities by 1.0 and 1.4 kcal/mol, respectively. The final CBS limit results are within about 0.3 kcal/mol of experiment in each case, which reflects the low intrinsic error of CCSD(T) for the electron affinities of the coinage metal elements.

The ionization potentials (IPs) shown in Table 4 for all the elements of the present work show excellent convergence with basis set and only small differences between the PP and all-electron DK approaches. Use of the diffuse augmented series of basis sets leads to improved convergence rates as was also noted previously in the all-electron first row transition metal study. This also seems to imply a relatively larger importance of sd correlation in the neutral atoms. The core-valence correlation contributions to the IPs are accurately predicted even with the cc-pwCVDZ-PP basis sets in these cases. After extrapolating both the valence-only and CV contributions to their respective CBS limits, the CCSD(T) IPs are all within 0.8 kcal/mol of experiment.

3.2 Molecular benchmark calculations

3.2.1 The coinage metal dimers: Cu₂, Ag₂, and Au₂

Due to their relatively simple electronic structure for transition metal dimers, the coinage metal homonuclear diatomics,

Table 2 Calculated CCSD(T) excitation energies $s^1d^{10} \rightarrow s^2d^9$ for the group 11 atoms compared to the J -averaged experimental values (kcal/mol)

Basis set ^a	Valence electrons correlated			Effect of $(n - 1)$ sp core-valence correlation		
	Cu	Ag	Au	Cu	Ag	Au
(VDZ/wCVDZ)-PP	21.99	89.40	40.75	-1.37	-8.98	-7.75
(VTZ/wCVTZ)-PP	28.83	92.34	42.13	-1.43	-8.06	-6.64
(VQZ/wCVQZ)-PP	31.67	94.60	43.70	-0.79	-7.39	-6.06
(V5Z/wCV5Z)-PP	32.75	95.21	44.14	-0.37	-6.88	-5.57
CBS(Q5)	33.86	95.85	44.59	0.06	-6.36	-5.06
(aVDZ/awCVDZ)-PP	30.79	93.37	42.22	-1.90	-8.94	-7.69
(aVTZ/awCVTZ)-PP	31.59	93.51	42.80	-1.01	-7.76	-6.45
(aVQZ/awCVQZ)-PP	32.94	94.94	43.90	-0.59	-7.29	-6.01
(aV5Z/awCV5Z)-PP	33.32	95.37	44.21	-0.26	-6.82	-5.54
CBS(Q5)	33.71	95.82	44.54	0.08	-6.33	-5.05
(aVTZ/awCVTZ)-DK	31.49	94.33	42.70	-0.10	-6.14	-4.88
(aVQZ/awCVQZ)-DK	32.87			0.33		
CBS(Val. + CV) ^b	33.8	89.5	39.5			
Expt. ^c	34.37	91.58	40.23			

^a Abbreviated as: $VnZ = cc-pVnZ$, $wCVnZ = cc-pwCVnZ$, $aVnZ = aug-cc-pVnZ$, $awCVnZ = aug-cc-pwCVnZ$ ($n = D, T, Q, 5$). The valence sets are used in the valence electrons correlated calculations, while the core-valence sets were used to determine the core-valence effects (valence and valence + outer-core calculations)

^b Obtained from the valence correlated and core-valence CBS limits (aVnZ series)

^c Ref. [88]

Table 3 Calculated CCSD(T) electron affinities for the group 11 atoms compared to the experimental values (kcal/mol)

Basis set ^a	Valence electrons correlated			Effect of $(n - 1)$ sp core-valence correlation		
	Cu	Ag	Au	Cu	Ag	Au
(aVDZ/awCVDZ)-PP	25.73	26.93	48.15	0.30	1.33	2.18
(aVTZ/awCVTZ)-PP	27.17	28.24	49.98	0.28	1.21	1.85
(aVQZ/awCVQZ)-PP	27.90	28.90	50.93	0.26	1.17	1.73
(aV5Z/awCV5Z)-PP	28.28	29.12	51.21	0.23	1.11	1.60
CBS(Q5)	28.61	29.30	51.42	0.20	1.04	1.46
(aVTZ/awCVTZ)-DK	27.31	28.26	50.43 ^b	0.21	0.98	1.41
(aVQZ/awCVQZ)-DK	28.04			0.18		
CBS(Val. + CV) ^c	28.8	30.3	52.9			
Expt. ^d	28.50	30.08	53.24			

^a Abbreviated as: $aVnZ = aug-cc-pVnZ$, $awCVnZ = aug-cc-pwCVnZ$ ($n = D, T, Q, 5$). The valence sets are used in the valence electrons correlated calculations, while the core-valence sets are used to determine the core-valence effects (valence and valence + outer-core calculations)

^b Contains a contribution of +0.40 kcal/mol for the difference between DK2 and DK3. See the text

^c Obtained from the valence correlated and core-valence CBS limits

^d Ref. [89]

especially Cu_2 and Au_2 , have been the subject of numerous theoretical studies. The most extensive previous study of the Au_2 ground state was by Hess and Kaldor [64], who utilized large basis sets and the all-electron scalar relativistic DK Hamiltonian with Møller–Plesset and CCSD(T) methods. This molecule was also recently addressed by Fleig and Visscher [65] using a spin-free Dirac–Coulomb Hamiltonian approach and CCSD(T). All three species have been studied recently by Hirao and coworkers [27] using the MP2 and CCSD(T) methods with the DK3 Hamiltonian. They utilized newly developed basis sets that were similar in size and accuracy to the $aug-cc-pVTZ-DK$ sets of the present work.

The present CCSD(T) results for the ground electronic states of the coinage metal dimers are shown in Tables 5, 6, and 7 for Cu_2 , Ag_2 , and Au_2 , respectively, using both the $cc-pVnZ-PP$ and $aug-cc-pVnZ-PP$ basis set series for valence-only correlation and the $cc-pwCVnZ-PP$ sets for the calculation of core-valence correlation effects. For all three

molecules the convergence rate of the spectroscopic constants is noticeably improved when the diffuse augmented sets are used, which would appear to reflect the importance of $d-d$ dispersion interactions. The resulting CBS limits are nearly the same, however, regardless of which basis set series is used.

The copper dimer exhibits the largest difference between the $cc-pVnZ-PP$ and $aug-cc-pVnZ-PP$ derived CBS limits, where the latter CBS limit for D_e is larger than the $cc-pVnZ-PP$ extrapolated value by 0.76 kcal/mol. The calculated core-valence correlation effects for Cu_2 are essentially zero, which agrees well with our previous all-electron study [12]. The effects of SO coupling are calculated to be completely negligible to the number of digits reported in Table 5. Upon comparing with the experiment, the final calculated spectroscopic constants for Cu_2 agree very well, with the equilibrium distance being a bit too short (-0.005 \AA) and the dissociation energy being slightly underestimated by about 0.6 kcal/mol.

Table 4 Calculated CCSD(T) ionization potentials for the group 11 and 12 atoms compared to the J -averaged experimental values (kcal/mol)

Basis set	Cu	Ag	Au	Zn	Cd	Hg
Valence-only						
cc-pVDZ-PP	165.26	163.05	200.23	211.18	200.71	231.33
cc-pVTZ-PP	171.89	168.06	206.05	212.71	202.01	234.78
cc-pVQZ-PP	174.89	170.69	208.08	214.50	203.97	236.52
cc-pV5Z-PP	176.47	171.88	209.08	215.42	204.83	237.33
CBS(Q5)	178.13	173.13	210.13	216.71	206.07	238.45
cc-pVTZ-DK	171.94	168.56	206.34 ^a	212.40	202.20	234.50 ^a
Effect of $(n - 1) sp$ correlation						
cc-pwCVDZ-PP	0.66	2.55	2.92	0.12	1.51	2.11
cc-pwCVTZ-PP	0.78	2.40	2.66	0.33	1.51	2.03
cc-pwCVQZ-PP	0.76	2.40	2.63	0.41	1.60	2.06
cc-pwCV5Z-PP	0.76	2.36	2.53	0.46	1.61	1.99
CBS(Q5)	0.75	2.32	2.42	0.50	1.62	1.92
cc-pwCVTZ-DK	0.66	1.97	2.11	0.25	1.25	1.53
CBS(Val. + CV) ^b	178.9	175.5	212.6	217.2	207.7	240.4
Expt. ^c	178.17	174.71	212.75	216.63	207.40	240.69

^a These contain contributions of +0.63 (Au) and +0.62 (Hg) kcal/mol for the differences between DK2 and DK3. See the text

^b Obtained from the valence correlated and core-valence CBS limits

^c Ref. [88,90]

Table 5 Calculated CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Cu₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)
Valence only					
	cc-pVDZ-PP	2.2375	264.8	1.13	45.21
	cc-pVTZ-PP	2.2319	260.5	1.11	43.69
	cc-pVQZ-PP	2.2251	263.3	0.99	44.55
	cc-pV5Z-PP	2.2186	266.1	1.02	45.35
	CBS(Q5) ^a	2.2147	268.8	1.04	45.86
	aug-cc-pVDZ-PP	2.2357	258.1	0.92	44.41
	aug-cc-pVTZ-PP	2.2213	266.1	1.03	45.39
	aug-cc-pVQZ-PP	2.2166	266.7	1.02	46.02
	aug-cc-pV5Z-PP	2.2154	267.7	1.02	46.36
	CBS(aQ5) ^a	2.2146	268.6	1.02	46.62
ΔCV ^b					
	cc-pwCVDZ-PP	0.0001	2.5	0.04	0.33
	cc-pwCVTZ-PP	0.0007	1.5	0.04	-0.02
	cc-pwCVQZ-PP	-0.0001	1.0	-0.01	-0.08
	cc-pwCV5Z-PP	-0.0004	1.3	0.01	-0.06
	CBS(wQ5) ^a	-0.0007	1.5	0.02	-0.04
ΔSO					
	aug-cc-pVTZ-PP	0.0000	0.0	0.00	0.00
	CBS(aQ5) + ΔCV + ΔSO	2.214	270.1	1.04	46.6
	Expt. ^c	2.2193	266.46	1.04	47.93±0.57

^a CBS extrapolation of the CCSD(T) correlation energy based on Eq. (1)

^b Effects of correlating the $(n - 1) sp$ electrons

^c Refs. [91,92]

The final calculated harmonic frequency is larger than the experimental value by $\sim 4 \text{ cm}^{-1}$, which is consistent with the slightly too short r_e . These results are nearly identical to the all-electron DK relativistic values of Ref. [12] that were otherwise calculated at the same level of theory.

In the case of the silver dimer (Table 6), the core-valence correlation effects are much larger than Cu₂, shortening r_e by 0.011 Å, increasing ω_e by 4.7 cm^{-1} , and increasing D_e by 0.9 kcal/mol at the CBS limit. The effect of SO coupling on the spectroscopic constants is very small, but larger than in Cu₂, i.e., r_e is decreased by 0.001 Å and D_e increased by 0.07 kcal/mol. The final CCSD(T) results shown in Table 6 when basis set incompleteness, core-valence correlation, and

SO coupling are taken into account agree well with the available experimental values. As in Cu₂, the bond length is slightly underestimated in the CCSD(T) valence + CV CBS limit (+SO) (-0.008 Å) and the harmonic frequency overestimated ($+4 \text{ cm}^{-1}$), but in the case of Ag₂ the calculated dissociation energy is actually a bit higher than the experimental value [66] and slightly outside of the stated experimental uncertainty. As discussed below, part of these differences can be attributed to small inaccuracies in the PP treatment with the remaining error being predominately intrinsic to the CCSD(T) method.

The present results for Au₂ shown in Table 7 exhibit similar trends as the other coinage metal dimers. In this case

Table 6 Calculated CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Ag₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)
Valence Only	cc-pVDZ-PP	2.5866	176.9	0.54	34.25
	cc-pVTZ-PP	2.5575	185.3	0.65	35.33
	cc-pVQZ-PP	2.5440	188.0	0.62	36.42
	cc-pV5Z-PP	2.5391	190.5	0.60	37.30
	CBS(Q5) ^a	2.5351	192.9	0.57	38.10
	aug-cc-pVDZ-PP	2.5675	182.7	0.59	35.79
	aug-cc-pVTZ-PP	2.5454	189.2	0.61	37.30
	aug-cc-pVQZ-PP	2.5377	190.9	0.62	38.03
	aug-cc-pV5Z-PP	2.5351	191.2	0.62	38.28
	CBS(aQ5) ^a	2.5339	191.5	0.62	38.45
ΔCV^b	cc-pwCVDZ-PP	-0.0113	5.2	-0.01	1.41
	cc-pwCVTZ-PP	-0.0110	4.9	0.00	1.00
	cc-pwCVQZ-PP	-0.0113	4.8	0.00	0.95
	cc-pwCV5Z-PP	-0.0111	4.8	0.02	0.93
	CBS(wQ5) ^a	-0.0108	4.7	0.04	0.91
ΔSO	aug-cc-pVTZ-PP	-0.0012	0.2	0.00	0.07
CBS(aQ5) + ΔCV + ΔSO		2.522	196.4	0.66	39.4
Expt. ^c		2.5303	192.40	0.64	38.0 ± 0.8

^a CBS extrapolation of the CCSD(T) correlation energy based on Eq. (1)^b Effects of correlating the $(n - 1)$ sp electrons^c Refs. [66,93,94]**Table 7** Calculated CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Au₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)
Valence only	cc-pVDZ-PP	2.5253	175.5	0.40	45.81
	cc-pVTZ-PP	2.5093	181.6	0.41	47.30
	cc-pVQZ-PP	2.4972	183.7	0.42	48.94
	cc-pV5Z-PP	2.4936	185.5	0.41	50.04
	CBS(Q5) ^a	2.4915	187.1	0.41	50.95
	aug-cc-pVDZ-PP	2.5203	180.2	0.43	47.39
	aug-cc-pVTZ-PP	2.5002	184.1	0.41	49.50
	aug-cc-pVQZ-PP	2.4946	185.6	0.41	50.52
	aug-cc-pV5Z-PP	2.4903	186.3	0.42	50.90
	CBS(aQ5) ^a	2.4876	186.9	0.42	51.15
ΔCV^b	cc-pwCVDZ-PP	-0.0119	4.9	-0.01	2.60
	cc-pwCVTZ-PP	-0.0106	4.0	-0.01	1.80
	cc-pwCVQZ-PP	-0.0104	3.8	0.00	1.61
	cc-pwCV5Z-PP	-0.0106	3.6	0.00	1.53
	CBS(wQ5) ^a	-0.0107	3.5	0.00	1.45
ΔSO	aug-cc-pVTZ-PP	-0.0049	1.1	0.00	0.62
CBS(aQ5) + ΔCV + ΔSO		2.472	191.5	0.42	53.2
Expt. ^c		2.4715	191.05	0.42	53.5 ± 0.1

^a CBS extrapolation of the CCSD(T) correlation energy based on Eq. (1)^b Effects of correlating the $(n - 1)$ sp electrons^c Refs. [94,96]

while the CBS limit dissociation energy is nearly the same regardless of which basis set series is used (cc-pVnZ-PP versus aug-cc-pVnZ-PP), the CBS limit bond length is about 0.004 Å shorter when the diffuse augmented series is used. The core-valence effects are very similar to those calculated for Ag₂ with a somewhat larger increase in D_e , 1.45 kcal/mol at the CBS limit. These CV effects are very similar to the counterpoise-corrected DK-CCSD(T) results reported previously by Hess and Kaldor [64] (for $5p5d6s$ correlation). In addition, the SO effects on the spectroscopic constants shown in Table 7, -0.0049 Å for r_e , 1.1 cm⁻¹ for ω_e , and 0.62 kcal/mol for D_e , are very similar to those obtained previously by van Lenthe et al. [67] (ZORA-GGA) and Lee

et al. [68] [REP-CCSD(T)], however the SO effect on D_e in this work is about 50% less than their values. The final CCSD(T)/CBS+CV+SO spectroscopic properties shown in Table 7 are in excellent agreement with the experimental values.

Table 8 shows the results of all-electron DK2 and DK3 calculations with explicit comparisons to the analogous PP-based results. On the one hand, use of the DK3 Hamiltonian is observed to yield nearly identical spectroscopic properties as those obtained at the DK2 level. The effect is completely negligible for Cu₂ and barely discernable for Ag₂. In the case of Au₂, the differences between the DK3 and DK2 values are just -0.0025 Å for r_e and $+0.25$ kcal/mol for

Table 8 Comparison of CCSD(T) all-electron DK and PP-based spectroscopic constants for Cu₂, Ag₂, and Au₂

	Basis ^a	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)
Valence-only					
Cu ₂	aug-cc-pwCVTZ-DK	2.2230	266.0	1.04	45.27
	Δ DK3 ^b	-0.0001	0.0	0.00	0.01
	Δ PP(val) ^c	0.0021	0.0	0.02	-0.09
Ag ₂	aug-cc-pwCVTZ-DK	2.5472	188.2	0.58	37.06
	Δ DK3 ^b	-0.0005	0.1	0.00	0.02
	Δ PP(val) ^c	0.0033	-0.3	-0.02	-0.17
Au ₂	aug-cc-pwCVTZ-DK	2.4977	184.4	0.43	49.63
	Δ DK3 ^b	-0.0025	0.6	-0.02	0.25
	Δ PP(val) ^c	-0.0016	0.7	-0.01	0.22
Val. + (n - 1) sp					
Cu ₂	aug-cc-pwCVTZ-DK	2.2233	267.1	1.04	45.17
	Δ PP(Δ CV) ^d	0.0010	-0.9	-0.03	-0.16
Ag ₂	aug-cc-pwCVTZ-DK	2.5380	192.4	0.61	37.87
	Δ PP(Δ CV) ^d	0.0031	-0.9	0.03	-0.33
Au ₂	aug-cc-pwCVTZ-DK	2.4898	187.4	0.43	50.93
	Δ PP(Δ CV) ^d	0.0041	-1.3	0.01	-0.72

^a The results using aug-cc-pwCV *n*Z-DK basis sets corresponded to all-electron calculations employing the second-order DKH Hamiltonian

^b Effects due to using the DK3 Hamiltonian compared to DK2. See the text

^c Difference between the all-electron DK3 (DK2 + Δ DK3) and PP-based results for valence-only correlation

^d Difference between the core-valence *effect* calculated with the all-electron DK2 method and those derived from PP calculations

D_e (DK3 - DK2 in each case). Of course the total energy is much lower in the DK3 calculations, $-41 E_h$ compared to DK2, but this is obviously of little practical importance for the properties of interest in this study. A limited number of tests on Au₂ comparing the DK3 and DK2 treatments of scalar relativity for core-valence correlation effects yielded completely negligible differences between the two. Using the CCSD(T) method also yielded results essentially identical to the MP2 values. As shown in Table 8, the differences between DK- and PP-based treatments for valence-only correlation, Δ PP(val), are relatively small, exhibiting maximum differences of just 0.003 Å for r_e (Ag₂) and 0.2 kcal/mol for D_e (Ag₂ and Au₂). For these strongly bound molecules, these results are expected to be stable with respect to further basis set extensions. Similar differences are also calculated for the core-valence correlation effects, where in general the PP-based calculations slightly overestimate the effects of correlating the (*n* - 1) *sp* electrons. Assuming additivity, the final CBS limit PP results of Tables 5-7 could be modified by the sum of the Δ PP(val) and Δ PP(Δ CV) values given in Table 8 to approximate all-electron CBS limit DK3 results (+SO). In particular, this would improve the agreement with experiment for Ag₂, especially for the equilibrium bond length.

It should also be mentioned that preliminary versions of the present basis sets have been used in benchmark-quality calculations on other strongly bound molecules with similar results in regards to accuracy as the present work [5, 69-71]. This is particularly evident in our previous calculations on the ground states of the diatomic gold halides [70], (AuF, AuCl, AuBr, and AuI), where nearly perfect agreement with experiment was obtained after basis set extrapolation and inclusion of both core-valence correlation and SO coupling effects.

3.2.2 The group 12 van der Waals dimers: Zn₂, Cd₂, and Hg₂

The group 12 dimers have been the subject of numerous theoretical and experimental studies due to their possible use as excimer laser substances. The ground states are only very weakly bound and the accuracy of the calculated spectroscopic properties are expected to show a strong dependence on the basis sets employed. The present results for Zn₂, Cd₂, and Hg₂ are shown in Tables 9, 10, and 11, respectively, where they are also compared to the available experimental values. In general, while the singly augmented (aug-cc-p*n*Z-PP) and doubly augmented (d-aug-cc-p*n*Z-PP) basis sets both lead to nearly identical CBS limits in each case, the d-aug series converge much more rapidly and the resulting spread between the CBS limits obtained with Eqs. (1) and (2) is much smaller.

Focusing first on the Zn dimer results in Table 9, a very strong dependence of the equilibrium bond length on basis set is observed. Even with the d-aug series of basis sets, extrapolation to the CBS limit leads to a decrease from the d-aug-cc-pV5Z-PP value of slightly more than 0.02 Å. The analogous difference between the CBS and aug-cc-pV5Z-PP values is 0.07 Å, but an identical CBS limit is obtained (with a much larger estimated uncertainty). This would appear to demonstrate the robustness of the present basis set extrapolation procedure. The two CBS limits for D_e are also within their estimated uncertainties. Core-valence correlation effects are calculated to have only a small effect on the derived spectroscopic properties of Zn₂, i.e., increasing r_e by 0.007 Å and decreasing D_e by just 3 cm⁻¹. The core-valence correlation effects on r_e and D_e calculated by Yu and Dolg [72], however, at the MP4 level of theory would appear to be

Table 9 Calculated counterpoise corrected^a CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Zn₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (cm ⁻¹)
Valence only	aug-cc-pVDZ-PP	4.3536	16.4	0.57	111.6 (101)
	aug-cc-pVTZ-PP	4.1932	17.6	0.54	131.3 (37)
	aug-cc-pVQZ-PP	4.0148	19.6	0.51	163.0 (27)
	aug-cc-pV5Z-PP	3.9132	21.9	0.56	193.0 (13)
	CBS ^b	3.840 [21]	23.9 [6]	0.59 [0]	221 [8]
	d-aug-cc-pVDZ-PP	4.2048	17.6	0.51	135.4 (120)
	d-aug-cc-pVTZ-PP	3.9538	21.1	0.54	183.7 (42)
	d-aug-cc-pVQZ-PP	3.8910	22.0	0.49	205.8 (39)
	d-aug-cc-pV5Z-PP	3.8619	23.1	0.54	218.1 (26)
	CBS ^b	3.840 [6]	24.0 [2]	0.56 [1]	229 [3]
	ΔCV	aug-cc-pwCVDZ-PP	0.0075	-0.1	0.03
aug-cc-pwCVTZ-PP		0.0071	-0.1	0.04	-2.5
aug-cc-pwCVQZ-PP		0.0068	-0.1	0.00	-2.9
ΔSO	aug-cc-pVTZ-PP	-0.0002	0.0	-0.02	0.0
CBS(daVnZ) + ΔCV + ΔSO		3.847	23.9	0.54	226
Expt. ^c		4.19	25.9±0.2	0.60±0.05	279.1

^a The BSSE removed by the counterpoise correction is given in parentheses for D_e

^b Obtained as the average of Q5 extrapolations using Eq. (1) and TQ5 extrapolations using Eq. (2). The estimated uncertainty in the extrapolation is given in square brackets for the last digit

^c Ref. [73]

Table 10 Calculated counterpoise corrected^a CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Cd₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (cm ⁻¹)
Valence only	aug-cc-pVDZ-PP	4.4438	13.3	0.24	152.4 (170)
	aug-cc-pVTZ-PP	4.1760	15.9	0.28	202.3 (48)
	aug-cc-pVQZ-PP	4.0002	18.6	0.27	261.4 (37)
	aug-cc-pV5Z-PP	3.9366	20.2	0.31	296.5 (17)
	CBS ^b	3.889[14]	21.5[4]	0.28[2]	327[9]
	d-aug-cc-pVDZ-PP	4.1794	16.8	0.28	219.6 (205)
	d-aug-cc-pVTZ-PP	3.9864	19.3	0.27	282.5 (74)
	d-aug-cc-pVQZ-PP	3.9318	20.5	0.32	307.6 (61)
	d-aug-cc-pV5Z-PP	3.9256	20.2	0.24	315.1 (32)
	CBS ^b	3.921[1]	20.0[1]	0.19[1]	321[2]
	ΔCV	aug-cc-pwCVDZ-PP	-0.0212	0.0	0.00
aug-cc-pwCVTZ-PP		-0.0205	0.1	-0.01	1.5
aug-cc-pwCVQZ-PP		-0.0239	0.2	0.00	3.4
ΔSO	aug-cc-pVTZ-PP	-0.0024	0.0	0.01	0.7
CBS(daVnZ) + ΔCV + ΔSO		3.894	20.2	0.20	325
Expt. ^c		4.07	23.0	0.40 ± 0.01	330.5

^a The BSSE removed by the counterpoise correction is given in parentheses for D_e

^b Obtained as the average of Q5 extrapolations using Eq. (1) and TQ5 extrapolations using Eq. (2). The estimated uncertainty in the extrapolation is given in square brackets for the last digit

^c Ref. [73]

strongly overestimated compared to these values. The inaccuracy of MP4 for this purpose was also noted in that same study based on additional CCSD(T) calculations. As also shown in Table 9, SO coupling effects are negligible for the Zn dimer.

Our final CCSD(T)/CBS+CV+SO results for the r_e and D_e of Zn₂ are in relatively poor agreement with the experimental values [72]. The experimental r_e , however, does not correspond to a directly measured quantity, but was derived based on modeling Zn₂ as a pure van der Waals molecule. As previously discussed by Yu and Dolg [72], however, all of the group 12 dimers have significant covalent contributions to their binding that would lead to a shortening of the bond length compared to a van der Waals interaction alone.

Recently the experimental equilibrium bond lengths of the group 12 dimers were re-evaluated by combining spectroscopic data and viscosity measurements [74]. The resulting value for Zn₂ (4.62 ± 0.05 Å), however, is longer than the previously cited experimental r_e and hence even further from the present predicted value. Furthermore, the predicted D_e of this work, 226 cm^{-1} , is more than 50 cm^{-1} below the experimental value. This is well outside the expected accuracy of the present calculations. The origin of this difference is not known at this time. Our results, however, are consistent with previous theoretical studies, notably the accurate calculations of Yu and Dolg [72] and the recent calculations of Ellingsen et al. [75]. The present work is the first to determine

Table 11 Calculated counterpoise corrected^a CCSD(T) spectroscopic properties of $X^1\Sigma_g^+$ Hg₂ as a function of basis set and compared to experiment

	Basis	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (cm ⁻¹)
Valence only	aug-cc-pVDZ-PP	4.2200	12.0	0.23	163.3 (217)
	aug-cc-pVTZ-PP	3.9367	15.7	0.21	263.7 (70)
	aug-cc-pVQZ-PP	3.8169	17.2	0.21	316.9 (34)
	aug-cc-pV5Z-PP	3.7689	18.4	0.22	349.9 (16)
	CBS ^b	3.733 [10]	19.4 [3]	0.22 [0]	378 [8]
	d-aug-cc-pVDZ-PP	4.0623	14.8	0.22	228.9 (262)
	d-aug-cc-pVTZ-PP	3.8368	17.5	0.22	317.4 (107)
	d-aug-cc-pVQZ-PP	3.7858	18.4	0.21	350.1 (58)
	d-aug-cc-pV5Z-PP	3.7530	18.5	0.21	361.5 (28)
	CBS ^b	3.725 [7]	18.7 [1]	0.23 [0]	371 [3]
Δ CV	aug-cc-pwCVDZ-PP	-0.0377	0.4	-0.01	8.3
	aug-cc-pwCVTZ-PP	-0.0344	0.5	0.01	13.1
	aug-cc-pwCVQZ-PP	-0.0385	0.6	0.01	17.0
Δ SO	aug-cc-pVTZ-PP	-0.0217	0.2	0.00	10.0
CBS(daVnZ) + Δ CV + Δ SO		3.665	19.5	0.24	398
Expt. ^c		3.63 ± 0.04	19.6 ± 0.3	0.26 ± 0.05	380 ± 15

^a The BSSE removed by the counterpoise correction is given in parentheses for D_e

^b Obtained as the average of Q5 extrapolations using Eq. (1) and TQ5 extrapolations using Eq. (2). The estimated uncertainty in the extrapolation is given in square brackets for the last digit

^c Value of r_e from Ref. [77], ω_e and $\omega_e x_e$ from Ref. [79], D_e from Ref. [78]. See Ref. [79] for other experimental values

CBS limits for these spectroscopic constants, and the present CBS+CV+SO values should be the most reliable to date for r_e , and perhaps even D_e .

The comparison of the present PP-based results and all-electron DK calculations are shown in Table 12 using d-aug QZ basis sets. As with the Cu₂ molecule, extensions of the DK Hamiltonian from second- to third-order leads to completely negligible differences in spectroscopic constants for Zn₂. By combining the valence-only and core-valence DK2-PP differences, Δ PP(val)+ Δ PP(Δ CV), the resulting estimated error from the pseudopotential approximation is also determined to be negligible in the present case.

The results for the Cd dimer shown in Table 10 exhibit similar trends as in Zn₂, although in general even more rapid convergence towards the CBS limit is observed with the d-aug series of basis sets as compared to Zn₂. This results in CBS limits for r_e that differ by about 0.03 Å depending on which basis set series (aug or d-aug) is used. The value obtained using the d-aug-cc-pVnZ-PP sets is certainly the most reliable. Contrastingly, the CBS limits for D_e are very similar between the two series, much like the case of Zn₂. Core-valence correlation effects are calculated to be relatively large for Cd₂ in regards to the bond length, i.e., -0.024 Å with the aug-cc-pwCVQZ-PP basis set, but they only lead to a modest increase in D_e with this same basis (+3.4 cm⁻¹). The inclusion of SO coupling slightly decreases r_e (-0.002 Å) and essentially leaves D_e unchanged. The final CBS+CV+SO values shown in Table 10 are in excellent agreement with the experimental dissociation energy [73], but the predicted r_e of this work (3.894 Å) is smaller than in the experiment. This latter value, however, was also modeled as a van der Waals molecule as in Zn₂ and is expected to be somewhat too long. The recently revised experimental value that incorporates viscosity measurements [74] is also much too long

(4.33 ± 0.05 Å). The best previous ab initio results were the CCSD(T) values of Yu and Dolg [72], and these were similar in quality to our current aug-cc-pV5Z-PP values. The comparisons between PP and DK calculations shown in Table 12 show the same trends as Zn₂. Both the valence-only and CV Δ PP values are of similar magnitude but opposite in sign, so that the total PP errors again appear to be negligible in this case.

The Hg dimer is the most extensively studied member of this series, both by theory and experiment. In particular, high resolution spectroscopy experiments [76–80] have resulted in accurate molecular parameters for the ground state. Recent ab initio studies include the work of Schwerdtfeger et al. [81,82], Munro et al. [83] and Dolg and Flad. [84]. In each of these cases the quasirelativistic PP of Häussermann et al. [32] was used with relatively large one-particle basis sets in order to minimize the basis set superposition error (BSSE). For example, the basis set used in the most recent work of Schwerdtfeger et al. [81] was optimized [85] at the MP2 level of theory and included up to h -type functions. In addition, Kunz et al. [86] reported all-electron calculations on Hg₂ employing the second-order DKH Hamiltonian. In each of these studies, high-level electron correlation methods were employed such as CCSD(T) and good agreement with the experiment was generally obtained, but the basis sets used did not allow an extrapolation to the CBS limit, which limited the accuracy attainable in these studies.

The results of the present work are shown in Table 11. The convergence of the counterpoise corrected spectroscopic properties is very regular with the d-aug-cc-pVnZ-PP series exhibiting the most rapid convergence with increasing n . Core-valence correlation effects are substantial, decreasing the bond length by 0.039 Å and increasing D_e by 17 cm⁻¹. Previous workers [82–84] had also investigated the effects

Table 12 Comparison of CP-corrected CCSD(T) all-electron DK and PP-based spectroscopic constants for Zn₂, Cd₂, and Hg₂

	Basis ^a	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (cm ⁻¹)
Valence-only Zn ₂	d-aug-cc-pVQZ-DK	3.8887	22.1	0.51	206.6
	Δ DK3 ^b	0.0000	0.0	0.00	0.0
	Δ PP(val) ^c	-0.0023	0.1	0.02	0.8
Cd ₂	d-aug-cc-pVQZ-DK	3.9259	20.3	0.29	309.2
	Δ DK3 ^b	0.0000	0.0	0.00	-0.2
	Δ PP(val) ^c	-0.0059	-0.2	-0.03	1.4
Hg ₂	d-aug-cc-pVTZ-DK	3.8275	17.1	0.19	319.6
	Δ DK3 ^b	-0.0028	0.0	0.00	-0.7
	Δ PP(val) ^c	-0.0121	-0.4	-0.03	1.4
Val. + (n - 1) sp Zn ₂	aug-cc-pwCVQZ-DK	3.9937	20.0	0.37	166.1
	Δ PP(Δ CV) ^d	0.0018	0.0	0.00	0.1
	Cd ₂	aug-cc-pwCVQZ-DK	3.9573	19.4	0.32
Hg ₂	Δ PP(Δ CV) ^d	0.0061	0.0	0.01	-0.6
	aug-cc-pwCVTZ-DK	3.8909	16.2	0.15	279.0
	Δ PP(Δ CV) ^d	0.0075	-0.1	-0.01	-2.4

^a The results using aug-cc-pwCVnZ-DK basis sets corresponded to all-electron calculations employing the second-order DKH Hamiltonian

^b Effects due to using the DK3 Hamiltonian compared to DK2. See the text

^c Difference between the all-electron DK3 (DK2 + Δ DK3) and PP-based results for valence-only correlation

^d Difference between the core-valence *effect* calculated with the all-electron DK2 method and those derived from PP calculations

of correlating the 5s and 5p electrons, but their results for the bond shortening due to core-valence correlation were all much too large, -0.1 Å at the MP4 level to -0.07 Å at the MP2 level. These results can mainly be attributed to using MPn methods for these systems, which are now known to strongly overestimate correlation effects in these cases. The CCSD(T) values of Yu and Dolg [72] ($\Delta r_e = -0.074$ Å and $\Delta D_e = 32$ cm⁻¹), while smaller than the MP4 results, are too large by about a factor of two, perhaps due to basis set effects. As shown in Table 11, SO coupling is estimated to decrease r_e by an additional 0.022 Å with an increase in D_e by 10 cm⁻¹. These values are similar to those obtained earlier by Dolg and Flad [84] using a two-electron PP ($\Delta r_e = -0.017$, $\Delta D_e = +8$ cm⁻¹), but smaller by about a factor of two from their 20-electron PP results. The CBS+CV+SO results shown in Table 11 should represent the most accurate theoretical values to date for this molecule. The predicted equilibrium bond length of 3.665 Å from this work is shorter than the experimental value obtained by simulations of the $G \leftarrow X$ electronic spectrum by Koperski et al. [80] 3.69 ± 0.01 Å, but within the stated uncertainty of the directly determined value of 3.63 ± 0.04 Å by van Zee et al. [77]. Curiously the experimentally derived value of Ref. [73], 3.66 ± 0.05 Å, is nearly identical to our predicted result for r_e . This is in strong contrast to their results for Zn₂ and Cd₂ as discussed above. In the case of D_e , as shown in Table 11 the predicted equilibrium binding energy from this work is just at the upper end of the experimental range.

Comparison of the PP-based results for Hg₂ with the corresponding DK values are given in Table 12. As observed previously for Au₂, the differences between results calculated with the DK3 and DK2 Hamiltonians are nearly negligible, i.e., differences of 0.0028 Å in r_e and 0.7 cm⁻¹ in D_e . Using basis sets of triple- ζ quality in the DK calculations, the valence-only result for r_e is slightly shorter in the

all-electron calculations compared to the PP values, while the binding energy is within 2 cm⁻¹. As observed for Zn₂ and Cd₂, the difference between the core-valence correlation effects determined in the DK and PP calculations are of similar magnitude as Δ PP(val), but opposite in sign. Hence the total apparent errors in the PP approximation, defined as the differences between the PP and DK3 results, are essentially negligible for all the spectroscopic constants evaluated for Hg₂ in this study.

Lastly, it should be particularly noted that the same pseudopotentials used in this work have been previously applied to the group 12 dimers by Figgen et al. [26] in benchmark CCSD(T) calculations. The basis sets they used in their study yielded spectroscopic properties intermediate between the present valence correlated d-aug-cc-pVTZ-PP and d-aug-cc-pVQZ-PP values. As suggested in their work and unambiguously confirmed in the present study by explicit basis set extrapolations and all-electron relativistic calculations, the resulting errors compared to the experiment that they observed should not be attributed to errors in the PP adjustment but to residual basis set truncation errors and incomplete electron correlation recovery.

4 Conclusions

Series of correlation consistent basis sets have been developed for the groups 11 and 12 elements based on recently reported relativistic pseudopotentials. Basis sets for both valence-only and outer-core electron correlation are reported, as well as these basis sets extended by diffuse functions. A limited number of relativistic all-electron basis sets of triple- ζ quality (and quadruple- ζ for Cd) were also optimized for each element of this study to provide accurate comparisons to the PP-based results. Large-scale atomic and molecular bench-

mark calculations were carried out at the CCSD(T) level of theory. Smooth, regular convergence towards the complete basis set limit was generally obtained when series of the new basis sets were used. This allowed for a systematic removal of basis set truncation errors, which was shown to be very important for approaching the experimental values as well as assessing the accuracy of the pseudopotential approximation. In general, excellent agreement with experiment was observed where available, and in the case of the group 12 van der Waals dimers, predictions for their equilibrium geometries were made in each case that are expected to be more accurate than the existing experimental results. Work is currently underway to extend these basis sets to the remaining elements of the transition metal block [33].

All of the basis sets presented in this work will be made available for download from the Pacific Northwest National Laboratory (PNNL) basis set website [87], as well as by request from one of the authors (KAP).

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