

Explicitly Correlated Coupled Cluster Calculations for Molecules Containing Group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) Elements: Optimized Complementary Auxiliary Basis Sets for Valence and Core–Valence Basis Sets

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S Supporting Information

ABSTRACT: Compact auxiliary basis sets matched to the standard aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP orbital basis sets have been developed for the coinage metals (Cu, Ag, Au) and group 12 elements (Zn, Cd, Hg) for use in the resolution of the identity (RI) approximation in explicitly correlated F12 calculations. The CCSD(T)-F12b method has been utilized with these auxiliary basis sets to carry out molecular benchmark calculations on homonuclear coinage metal diatomics (Cu₂, Ag₂, Au₂), as well as mono- (CuF, AgF, AuF) and difluorides (CuF₂, AgF₂, AuF₂). The resulting equilibrium geometries, harmonic vibrational frequencies, and atomization energies demonstrate that CCSD(T)-F12b calculations using double- ζ -quality basis sets produce results comparable in accuracy to conventional CCSD(T) quadruple- ζ calculations, while F12b with triple- ζ -quality sets yields results close to 5- ζ , which is near the conventional complete basis set (CBS) limit estimates. Analogous trends are observed for the group 12 monofluorides (ZnF, CdF, HgF). It is also shown that the effects of correlating the transition metal element ($n - 1$)s and p electrons are relatively insensitive to the size of the basis set when the F12 method is utilized.

I. INTRODUCTION

The application of high accuracy *ab initio* methods to compounds containing transition metal elements has long lagged behind that of molecules containing main group elements. Initially, this was partially due to a lack of appropriate basis sets, either all-electron or those paired with small-core relativistic pseudopotentials. This has been remedied with the development of systematically convergent correlation consistent (cc) basis sets for all three rows of the transition metal block of the periodic table.^{1–4} Most of these latter basis sets involve the use of Stuttgart-style small-core relativistic pseudopotentials. Of course, the electronic structures of molecules containing transition metals are often complicated due to their high density of states, leading in particular to strong multireference effects and a need to use highly correlated methods to obtain accurate results. The latter methods, e.g., coupled cluster (CC) or multi-reference configuration interaction (MRCI), scale steeply with both the system size and the number of correlated electrons, which can severely limit the size of transition metal complexes that can be accurately treated.

Given the difficulties in treating transition metal complexes with high-level *ab initio* methods, it is especially problematic that total energies and properties of such systems often converge slowly with respect to basis set size. To illustrate this with an example, previous work has shown that for the ground electronic state of the gold dimer, the CCSD(T)/aug-cc-pVDZ-PP spectroscopic properties lie far from estimates of the complete basis set (CBS) limit ($R_e = 2.488$ Å, $\omega_e = 186.9$ cm^{−1}, $D_e = 51.2$ kcal mol^{−1}).² The equilibrium bond length is too long by 0.033 Å, the harmonic frequency too small by 6.7 cm^{−1}, and the dissociation energy is underestimated by 3.8 kcal mol^{−1}. Given the steep scaling of the CCSD(T) method ($n^2N^4N_{it}$, plus a

single n^3N^4 step, with n , N , and N_{it} denoting the numbers of occupied molecular orbitals, virtual orbitals, and CCSD iterations, respectively), it is easy to envisage that aug-cc-pVDZ-PP sized basis sets may be the only feasible choice for small to moderately sized transition metal complexes, without resorting to less rigorous methods. However, recent developments in methods that include terms in the wave function that depend explicitly on the interelectronic distance, so-called explicitly correlated methods, have demonstrated a dramatic improvement in convergence with respect to the basis set with a computational cost that is only slightly higher than the analogous conventional method. These techniques, such as the explicitly correlated coupled cluster singles and doubles with perturbative triples CCSD(T)-F12b method^{5,6} or MRCI-F12,⁷ should represent an attractive and efficient route to producing high accuracy *ab initio* structures, thermochemistry, and spectroscopic properties for compounds containing transition metal elements, since they will allow accurate studies of this type to be carried out with much smaller basis sets, e.g. double- ζ , than are required for conventional calculations (QZ and above). This in turn should allow much larger complexes to be treated. The interested reader can find detailed background, benchmarks, and references for explicitly correlated methods in recent reviews.^{8–10}

The additional complexity of an explicitly correlated calculation generally means that three auxiliary basis sets (ABSs) are required in addition to the normal orbital basis set (OBS) that is needed in a conventional *ab initio* calculation. Two of these auxiliary sets are utilized in the robust density fitting (DF) of

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the Fock and exchange matrices, as well as the remaining two electron integrals. The same ABSs used in DF-HF^{11,12} and DF-MP2,^{13,14} respectively, have been demonstrated to be good choices. The third ABS is used in resolution of the identity (RI) approximations to reduce the computationally expensive three- and four-electron integrals arising from the explicitly correlated terms to products of at most two-electron integrals. The introduction of the RI approximation by Kutzelnigg and Klopper^{15,16} in the context of MP2-R12 was the breakthrough that made explicitly correlated methods practical for general use. In the present context, this is accurately performed by combining the ABS and orbital basis set in the complementary auxiliary basis set (CABS) approach,¹⁷ which is then used as the RI basis. Over the past few years, progress has been made in the design and optimization of ABSs specifically for this purpose, denoted OptRI. These ABSs provide only functions complementary to the chosen orbital basis sets to ensure that no linearly dependent functions arise, and hence they are also compact for computational efficiency. OptRI basis sets thus far have been matched to the cc-pVnZ-F12 and cc-pCVnZ-F12 OBSs for the elements H–Ar^{18–20} and to the aug-cc-pVnZ OBSs for H, He, B–Ne, and Al–Ar.²¹ Optimization of OptRI auxiliary sets for new pseudopotential-based F12 basis sets has also recently been carried out for all of the post-d elements Ga–Rn (to be published), with recent CCSD(T)-F12b benchmark calculations using these sets reported for post-3d elements.²² To simplify the selection of auxiliary basis sets, modern quantum chemistry packages featuring explicitly correlated methods provide sensible default choices, such that the user only needs to select an OBS for main group elements.

In the present work, new aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP ($n = \text{D, T, Q, 5}$) OptRI auxiliary basis sets are developed to match the equivalently named orbital basis sets for the six elements Cu through Au and Zn through Hg. These new OptRI sets are then employed in CCSD(T)-F12b calculations that display rapid convergence toward the CBS limit for molecular geometries, harmonic frequencies, and dissociation energies for a few small molecules containing group 11 and 12 elements.

II. GENERAL COMPUTATIONAL DETAILS

All explicitly correlated calculations were performed with the MOLPRO^{23,24} package of *ab initio* programs. Coupled cluster calculations were carried out with the CCSD(T)-F12b method,⁵ utilizing R/UCCSD(T)-F12b for open shell species.^{6,25} The latter method employs restricted open shell HF orbitals but is spin unrestricted in the CCSD equations. The fixed amplitude, diagonal *Ansatz* 3C(FIX)²⁶ was used throughout. The pseudopotential-based correlation consistent basis sets augmented with diffuse functions, aug-cc-pVnZ-PP ($n = \text{D, T, Q, 5}$), of Peterson and Puzarini² were used as the atomic orbital basis sets in the frozen-core calculations, along with the small-core (10 electrons for Cu/Zn, 28 electrons for Ag/Cd, and 60 electrons for Au/Hg) relativistic pseudopotentials of Figgen et al.²⁷ This combination will be abbreviated as aVnZ-PP herein. Density fitting (DF) of the Fock and exchange matrices used the def2-QZVPP/JKFIT auxiliary basis sets (ABSs) of Weigend,²⁸ while DF of the remaining two-electron integrals employed the aug-cc-pVnZ-PP/MP2FIT basis of Hättig and Hellweg.²⁹ It should be noted that density fitting is only used for quantities normally appearing in the MP2-F12 method; i.e., density fitting is not used for quantities specific to CCSD. The RI approximation utilized the CABS procedure¹⁷

using the OptRI ABSs developed as part of this investigation (see section III.B). Initially the values of the geminal Slater exponent, β , were taken from previous work³⁰ on first and second row p-block elements, i.e., 0.9, 1.0, 1.0, and $1.0 a_0^{-1}$ for $n = \text{D, T, Q, 5}$, respectively. The resulting basis set convergence for the calculated bond lengths, however, was much less impressive than the trends observed for the cases where the outer-core electrons were correlated. These latter cases used a β value of $1.4 a_0^{-1}$ throughout (see below). The frozen-core calculations were then repeated with $\beta = 1.4 a_0^{-1}$, which resulted in a much improved basis set convergence for the bond lengths, while the dissociation energies obtained using basis sets larger than DZ were nearly unaffected. The results of these latter calculations appear in the tables of this paper that are discussed below, while the results with the smaller β values can be found in the Supporting Information.

The effect of correlating the $(n - 1)$ s and p outer-core electrons of the metals (i.e., all electrons not replaced by the pseudopotential) on the spectroscopic parameters was probed using the weighted core–valence correlation consistent basis sets, aug-cc-pwCVnZ-PP (denoted awCVnZ-PP), along with the aug-cc-pwCVnZ-PP/MP2FIT ABSs. The auxiliary basis sets for the Fock matrix remained the same as in the valence-only calculations, with the awCVnZ-PP/OptRI sets developed within this investigation utilized for the RI. The geminal Slater exponent was set to $1.4 a_0^{-1}$ in these cases.

To benchmark the new auxiliary basis sets as well as the performance of the CCSD(T)-F12b method for these transition metal elements, near-equilibrium potential energy functions were calculated for the coinage metal dimers (Cu_2 , Ag_2 , and Au_2), fluorides (CuF , AgF , AuF , ZnF , CdF , and HgF), and difluorides (CuF_2 , AgF_2 , and AuF_2). For the diatomics, this was facilitated by sixth-degree polynomial fits to a series of seven energies distributed around the equilibrium geometries ($-0.3 a_0 \leq R - R_e \leq +0.5 a_0$). Spectroscopic parameters were then evaluated using a Dunham analysis.³¹ In the case of the linear, centrosymmetric difluorides, the equilibrium metal–fluorine bond lengths were obtained in the same manner as in the diatomic cases. The cc-pVnZ-F12 ($n = \text{D, T, Q}$) series of orbital basis sets³² were employed for the fluorine atom, along with the aVnZ/MP2FIT,³³ VnZ/JKFIT,¹¹ and cc-pVnZ-F12/OptRI¹⁸ ABSs. The 1s electrons on the fluorine atoms were treated with the frozen core approximation throughout. For both fluorine and the transition metal elements, the DZ orbital basis sets were paired with the TZ/MP2FIT ABSs, as recommended elsewhere.³⁰ Similarly, the DZ orbital basis for fluorine was paired with the TZ/JKFIT ABS.

In order to assess the basis set convergence of the CCSD(T)-F12b method, conventional CCSD(T) calculations were also carried out with the aVnZ-PP and awCVnZ-PP basis sets on the metals with aug-cc-pVnZ utilized for F. The frozen-core results for the coinage metal dimers were taken from ref 2. Analogous to this latter work, estimated complete basis set (CBS) limits for both frozen-core and 3s3p correlation were obtained by combining the 5Z Hartree–Fock (HF) energies at each geometry with QZ and 5Z CCSD(T) correlation energies extrapolated via the usual $1/n^3$ formula,³⁴ where n corresponded to the cardinal number of the basis set ($n = 4$ or 5) in all cases. Alternative extrapolation schemes utilizing different choices of n , e.g., $n + 1$ (corresponding to l_{max} for the transition metals) or $n + 1/2$ (a compromise between the l_{max} of the transition metals and that of F), were not investigated in the present work.

III. BASIS SET DEVELOPMENT

A. Calibration of Density Fitting. As is apparent from considering atomic calculations, for DF-MP2 the MP2FIT ABS should contain functions with an angular momentum at least equal to $l_{\text{occ}} + l_{\text{AO}}$, where l_{occ} is the highest angular momentum occupied in the ground state of the atom and l_{AO} is the highest angular momentum in the orbital basis set. This ensures that the ABS accurately represents orbital products involving one occupied orbital and one virtual orbital. In the present case of the transition metals, this would require k functions for the aVQZ-PP set and l functions for the aVSZ-PP set, neither of which are currently supported in MOLPRO. It has been documented that simply truncating the MP2FIT sets to the largest supported angular momentum leads to significant density fitting errors, as defined by the difference in the conventional MP2 and DF-MP2 correlation energies.³⁵ However, it has not been established whether this error is constant, thus canceling for relative energies, or if it is more random in nature. In order to investigate this, near-equilibrium potential energy functions for both Cu_2 and CuF_2 were calculated as described above using MP2 and DF-MP2. The resulting bond lengths (R_e) and dissociation energies (D_e and ΣD_e), as well as harmonic frequencies (ω_e) for Cu_2 , are presented in Table 1. In the

Table 1. MP2 Spectroscopic Constants and Their DF Fitting Errors for $X^1\Sigma_g^+ \text{Cu}_2$ and $X^2\Sigma_g^+ \text{CuF}_2$ ^a

| molecule | method | basis set | R_e (Å) | ω_e (cm^{-1}) | ΣD_e (kcal mol^{-1}) |
|----------------|----------|-----------|-----------|---------------------------------|---|
| Cu_2 | MP2 | aVDZ-PP | 2.2110 | 277.5 | 44.80 |
| | | aVTZ-PP | 2.1982 | 284.8 | 46.45 |
| | | aVQZ-PP | 2.1930 | 286.1 | 47.44 |
| | | aVSZ-PP | 2.1919 | 286.9 | 47.86 |
| | DF error | aVDZ-PP | 0.0000 | 0.0 | 0.00 |
| | | aVTZ-PP | 0.0000 | 0.0 | 0.00 |
| | | aVQZ-PP | 0.0000 | 0.0 | −0.01 |
| | | aVSZ-PP | 0.0001 | −0.1 | −0.01 |
| CuF_2 | MP2 | aVDZ-PP | 1.7254 | | 170.33 |
| | | aVTZ-PP | 1.7133 | | 175.35 |
| | | aVQZ-PP | 1.7105 | | 177.41 |
| | | aVSZ-PP | 1.7096 | | 177.98 |
| | DF error | aVDZ-PP | 0.0000 | | 0.02 |
| | | aVTZ-PP | 0.0000 | | 0.01 |
| | | aVQZ-PP | 0.0000 | | −0.09 |
| | | aVSZ-PP | 0.0000 | | −0.14 |

^aThe aVQZ-PP/MP2FIT and aVSZ-PP/MP2FIT ABSs were truncated at i -type functions.

case of Cu_2 , it can be seen that DF-MP2 gives essentially the same results as conventional MP2 with all basis sets; R_e differs at most by 0.0001 Å, ω_e by 0.1 wavenumber, and D_e by 0.01 kcal mol^{-1} . The largest DF errors occur for the aVSZ-PP basis set. Thus, truncating the ABSs for aVQZ-PP and aVSZ-PP apparently has no effect on these three properties of Cu_2 . The trend is slightly different for the atomization energy of CuF_2 , which involves a change in the oxidation state of the metal. While the DF errors are negligible for the DZ and TZ basis sets, those for ΣD_e increase to 0.09 and 0.14 kcal mol^{-1} for QZ and SZ, respectively. Hence, while the lack of k functions in the QZ ABS is not a significant problem, the lack of both k and l functions from the SZ ABS does begin to be relevant for high accuracy work in this particular case. In contrast, analogous

tests for the core–valence correlation effects on these properties of Cu_2 and CuF_2 carried out with the awCVnZ-PP basis sets exhibited negligible differences (largest DF error of 0.03 kcal mol^{-1} for the $\Delta \Sigma D_e$ of CuF_2). As another example, the DF error in the correlation energy for a neutral Au atom with the VSZ-PP basis set is 2.106 mE_h , while that for the Au^{3+} cation is 1.160 mE_h . This corresponds to a DF error of about 0.6 kcal mol^{-1} between the two oxidation states.

B. Development of RI Auxiliary Basis Sets. RI auxiliary basis sets for use in the CABS procedure¹⁷ within F12 calculations as implemented^{36,37} in MOLPRO have previously been reported for use with the lighter first and second row elements, H–Ar.^{18–21} The two main features of these OptRI sets are that they are explicitly matched to a particular AO basis set (helping to ensure smooth potential energy surfaces and numerical stability within the CABS approach) and that the sets are compact (for reduced computational cost). Following the established procedure^{18,21} for the design and optimization of OptRI ABSs, new OptRI sets for the elements Cu, Zn, Ag, Cd, Au, and Hg have been developed to match the aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP orbital basis sets using the MP2-F12 method (using $\beta = 1.4 a_0^{-1}$). The reference RI set required for this procedure was a large even-tempered 18s17p16d12f10g8h7i ABS. The compositions of the resulting OptRI sets are detailed in Table 2, with the exponents explicitly given as part of the

Table 2. Number and Type of Functions Included in the OptRI ABSs Optimized in This Work to Be Used within the CABS Framework with Their Associated AO Basis Sets

| basis set | functions |
|------------------------|----------------|
| aug-cc-pVDZ-PP/OptRI | 6s6p6d5f4g2h1i |
| aug-cc-pVTZ-PP/OptRI | 7s6p6d5f5g4h1i |
| aug-cc-pVQZ-PP/OptRI | 6s6p6d5f4g5h2i |
| aug-cc-pVSZ-PP/OptRI | 6s7p6d6f4g3h4i |
| aug-cc-pwCVDZ-PP/OptRI | 5s5p5d4f4g2h1i |
| aug-cc-pwCVTZ-PP/OptRI | 5s4p4d4f4g4h1i |
| aug-cc-pwCVQZ-PP/OptRI | 4s4p4d4f4g4h2i |
| aug-cc-pwCVSZ-PP/OptRI | 4s5p4d5f4g3h3i |

Supporting Information. It should be noted that as in the case of the MP2FIT ABSs discussed above, the OptRI auxiliary sets are also limited to a maximum angular momentum of i -type functions. It is not clear in this case how to test the impact of this restriction. However, the accurate results shown below for the molecular benchmark calculations would seem to indicate that any remaining incompleteness in the RI basis does not lead to significant errors.

In the present case, the aug-cc-pwCVnZ-PP/OptRI basis sets were first optimized in calculations where all of the electrons outside the PP were correlated. Then, the aug-cc-pVnZ-PP/OptRI ABSs were defined by simply combining the core-correlating functions of the corresponding aug-cc-pwCVnZ-PP orbital basis sets with the aug-cc-pwCVnZ-PP/OptRI sets, which would ensure that the same exponent space was spanned by both RI sets. However, for all sets larger than DZ, some of the valence correlating functions in the awCVnZ-PP orbital basis sets were not identical to those in aVnZ-PP.² This meant that for the aVTZ-PP set the f functions in the OptRI set needed to be reoptimized; the f and g functions for aVQZ-PP; and f , g , and h functions for aVSZ-PP. It should also be noted that the p functions for the aug-cc-pVQZ-PP/OptRI set also had to be

reoptimized to prevent functions being deleted in the CABS procedure.

Statistics of the RI errors in the MP2-F12 correlation energies, defined in this case as the difference when using the OptRI ABSs relative to the reference RI ABS, are displayed in Table 3 (using $\beta = 0.9, 1.0, 1.0, 1.0 a_0^{-1}$ for DZ, TZ, QZ, SZ,

Table 3. RI Errors (Relative to the Reference RI) in the MP2-F12/3C(FIX) Correlation Energies Obtained with the OptRI ABSs Developed in This Work for a Test Set of 21 Systems^a

| orbital basis | auxiliary basis | MUD | σ | MAX |
|---------------|------------------------|-----------|-----------|------------|
| aVDZ-PP | reference ^b | (45564.7) | (29780.5) | (130237.3) |
| | aVDZ-PP/OptRI | 671.0 | 358.8 | 1528.2 |
| aVTZ-PP | reference ^b | (15396.4) | (8734.4) | (38217.1) |
| | aVTZ-PP/OptRI | 423.4 | 209.4 | 1085.0 |
| aVQZ-PP | reference ^b | (6647.8) | (3362.8) | (14287.7) |
| | aVQZ-PP/OptRI | 70.1 | 62.3 | 294.8 |
| aVSZ-PP | reference ^b | (2394.5) | (886.8) | (4804.6) |
| | aVSZ-PP/OptRI | 13.8 | 10.1 | 42.2 |

^aThe cc-pVnZ-F12 series of OBSs and OptRI ABSs were employed for fluorine ($n = 4$ was used in combination with the $n = 5$ basis set on the transition metal). All values are in μE_h . MUD is the mean unsigned deviation; σ , the standard deviation; and MAX, the maximum unsigned deviation. ^bBasis set truncation errors in the correlation energy for the given combination of OBS and reference RI ABS. The CBS limit has been estimated as the MP2-F12/awCVSZ-PP correlation energy using the reference RI ABS. Only the valence electrons were correlated in these estimates.

respectively). The unsigned deviation, standard deviation, and maximum unsigned deviation are reported for a test set of 21 atoms, cations, and diatomics: Cu, Cu²⁺, Ag, Ag⁺, Au, Au³⁺, Zn, Zn⁺, Cd, Cd⁺, Hg, Hg⁺, Cu₂, Ag₂, Au₂, CuF, AgF, AuF, ZnF, CdF, and HgF. Table 3 also shows the OBS incompleteness error, estimated by assuming that MP2-F12/awCVSZ-PP correlation energies using the reference RI ABS are close to the CBS limit (the VQZ-F12 OBS and OptRI ABS were employed for fluorine). While the RI errors may initially seem large, Table 3 clearly shows that the RI errors due to the use of the OptRI ABSs are typically 2 orders of magnitude smaller than the orbital basis set truncation error, reflecting the slow convergence of correlation energy with basis set size for transition metals. As expected, the statistics of the errors due to the OptRI ABSs decreases as the size of the basis set increases, with errors at the aVSZ-PP/OptRI level more than an order of magnitude smaller than at the aVDZ-PP/OptRI or aVTZ-PP/OptRI level.

As a further test of the suitability of the OptRI ABSs, Table 4 lists bond lengths (R_e), harmonic frequencies (ω_e), and dissociation energies (D_e) resulting from near-equilibrium potential energy scans using CCSD(T)-F12b for both Cu₂ and CuF. All electrons were correlated, and $\beta = 1.4 a_0^{-1}$. The scans were carried out using the reference RI ABS and then repeated with the OptRI sets developed in this work (the OptRI sets were employed for fluorine in all cases). It can be seen that the largest RI errors result from the awCVDZ-PP set, with R_e differing by 0.0011 Å, ω_e by almost one wavenumber, and D_e by up to 0.2 kcal mol⁻¹. An inspection of the basis set effect on the spectroscopic constants indicates that the awCVDZ-PP results are sufficiently far from the basis set limit that errors of the above magnitude are not a cause for concern. As the size of the orbital basis set is increased, the associated RI error in using

Table 4. CCSD(T)-F12b Spectroscopic Constants (RefRI) and Their RI Errors (OptRI) for the X¹Σ_g⁺ State of Cu₂ and X¹Σ⁺ State of CuF^a

| molecule | basis set | RI basis | R_e (Å) | ω_e (cm ⁻¹) | D_e (kcal mol ⁻¹) |
|-----------------|-----------|----------|-----------|--------------------------------|---------------------------------|
| Cu ₂ | awCVDZ-PP | RefRI | 2.2149 | 268.1 | 46.13 |
| | awCVTZ-PP | | 2.2127 | 269.7 | 46.28 |
| | awCVQZ-PP | | 2.2119 | 269.4 | 46.43 |
| | awCVSZ-PP | | 2.2119 | 269.9 | 46.59 |
| | awCVDZ-PP | OptRI | -0.0011 | 0.0 | 0.20 |
| | awCVTZ-PP | | -0.0001 | 0.2 | 0.04 |
| | awCVQZ-PP | | -0.0001 | -0.1 | 0.01 |
| | awCVSZ-PP | | -0.0001 | -0.1 | 0.01 |
| CuF | awCVDZ-PP | RefRI | 1.7460 | 613.2 | 100.23 |
| | awCVTZ-PP | | 1.7447 | 617.1 | 98.44 |
| | awCVQZ-PP | | 1.7442 | 618.2 | 98.32 |
| | awCVSZ-PP | | 1.7441 | 618.3 | 98.33 |
| | awCVDZ-PP | OptRI | -0.0011 | 0.8 | 0.16 |
| | awCVTZ-PP | | 0.0000 | 0.2 | -0.03 |
| | awCVQZ-PP | | -0.0001 | 0.1 | -0.01 |
| | awCVSZ-PP | | 0.0000 | 0.0 | -0.01 |

^aAll Cu electrons were correlated (except those replaced by the pseudopotential), and the cc-pVnZ-F12 orbital and RI basis sets were used on fluorine ($n = 4$ was used in combination with the $n = 5$ basis set on the transition metal).

the OptRI ABSs becomes negligible as the results are essentially the same as those produced with the reference RI set. The effect of the RI auxiliary basis on the spectroscopic constants of AgF and AuF are presented in Table SI in the Supporting Information, where the RI errors are approximately of the same size as those for CuF.

IV. MOLECULAR BENCHMARK CALCULATIONS

The CCSD(T)-F12b results for R_e , ω_e , and D_e are shown in Table 5 for the electronic ground states of the coinage metal dimers Cu₂, Ag₂, and Au₂. These values are compared to the conventional CCSD(T)/aVnZ-PP results of Peterson and Puzzarini,² as well as new CCSD(T)/awCVnZ-PP results, all with estimated CBS limits. An inspection of the conventional data indicates that the convergence is slow but relatively monotonic. Results obtained with 5Z quality sets are relatively close to their respective CBS limits, e.g., within a few thousandths of an Angstrom for R_e and a few tenths of a kcal mol⁻¹ for D_e . The convergence also appears to be slower for elements further down the group, i.e., Au₂ compared to Cu₂. As expected, the explicitly correlated results display a much faster convergence toward the CBS limit than the values obtained using the conventional method. The F12b ansatz with DZ basis sets produces results with a quality somewhere between conventional TZ and QZ. In general, the TZ F12b values are approximately of 5Z quality and hence close to the conventional CBS limits. These trends are shown in Figure 1 for the dissociation energy of Au₂. Given the slow basis set convergence of the conventional results, the CCSD(T)-F12b/aVSZ-PP spectroscopic parameters should act as more accurate estimates of the CBS limit than those from extrapolation in these cases.

Due to the poor performance of CCSD(T)/aVDZ-PP for coinage metal dimers shown in Table 5, it is reassuring that the F12 method with the same basis set produces results that are significantly closer to estimates of the CBS limit. Recalling the example of the gold dimer detailed in the Introduction,

Table 5. Calculated Spectroscopic Constants for the $X^1\Sigma_g^+$ States of Cu_2 , Ag_2 , and Au_2 ^a

| system | method | basis set | R_e (Å) | ω_e (cm^{-1}) | D_e (kcal mol^{-1}) | basis set | R_e (Å) | ω_e (cm^{-1}) | D_e (kcal mol^{-1}) |
|---------------|----------------------|-------------------------|-----------|---------------------------------|----------------------------------|-----------|-----------|---------------------------------|----------------------------------|
| Cu_2 | CCSD(T) ^b | aVDZ-PP ^b | 2.2357 | 258.1 | 44.41 | awCVDZ-PP | 2.2343 | 262.5 | 44.80 |
| | | aVTZ-PP ^b | 2.2213 | 266.1 | 45.39 | awCVTZ-PP | 2.2201 | 267.9 | 45.42 |
| | | aVQZ-PP ^b | 2.2166 | 266.7 | 46.02 | awCVQZ-PP | 2.2143 | 268.1 | 45.96 |
| | | aVSZ-PP ^b | 2.2154 | 267.7 | 46.36 | awCVSZ-PP | 2.2127 | 269.6 | 46.43 |
| | | CBS(aQ5) ^b | 2.2146 | 268.6 | 46.62 | CBS(awQ5) | 2.2113 | 270.9 | 46.89 |
| | CCSD(T)-F12b | aVDZ-PP | 2.2158 | 265.8 | 46.27 | awCVDZ-PP | 2.2138 | 268.1 | 46.33 |
| | | aVTZ-PP | 2.2140 | 268.5 | 46.38 | awCVTZ-PP | 2.2126 | 269.9 | 46.32 |
| | | aVQZ-PP | 2.2137 | 268.1 | 46.52 | awCVQZ-PP | 2.2118 | 269.3 | 46.44 |
| | | aVSZ-PP | 2.2132 | 268.5 | 46.67 | awCVSZ-PP | 2.2119 | 269.8 | 46.60 |
| | | experiment ^c | | | | | 2.2193 | 266.46 | 47.93 ± 0.57 |
| Ag_2 | CCSD(T) | aVDZ-PP ^b | 2.5675 | 182.7 | 35.79 | awCVDZ-PP | 2.5491 | 189.7 | 37.41 |
| | | aVTZ-PP ^b | 2.5454 | 189.2 | 37.30 | awCVTZ-PP | 2.5312 | 193.8 | 38.38 |
| | | aVQZ-PP ^b | 2.5377 | 190.9 | 38.03 | awCVQZ-PP | 2.5218 | 196.8 | 39.22 |
| | | aVSZ-PP ^b | 2.5351 | 191.2 | 38.28 | awCVSZ-PP | 2.5223 | 196.4 | 39.37 |
| | | CBS(aQ5) ^b | 2.5339 | 191.5 | 38.45 | CBS(awQ5) | 2.5232 | 195.9 | 39.50 |
| | CCSD(T)-F12b | aVDZ-PP | 2.5399 | 188.8 | 37.69 | awCVDZ-PP | 2.5248 | 194.6 | 38.78 |
| | | aVTZ-PP | 2.5343 | 191.6 | 38.25 | awCVTZ-PP | 2.5209 | 196.2 | 39.24 |
| | | aVQZ-PP | 2.5323 | 192.0 | 38.55 | awCVQZ-PP | 2.5189 | 197.3 | 39.54 |
| | | aVSZ-PP | 2.5321 | 192.1 | 38.62 | awCVSZ-PP | 2.5202 | 196.6 | 39.55 |
| | | experiment ^c | | | | | 2.5303 | 192.40 | 38.0 ± 0.8 |
| Au_2 | CCSD(T) | aVDZ-PP ^b | 2.5203 | 180.2 | 47.39 | awCVDZ-PP | 2.5041 | 185.8 | 50.23 |
| | | aVTZ-PP ^b | 2.5002 | 184.1 | 49.50 | awCVTZ-PP | 2.4848 | 188.7 | 51.68 |
| | | aVQZ-PP ^b | 2.4946 | 185.6 | 50.52 | awCVQZ-PP | 2.4814 | 189.6 | 52.33 |
| | | aVSZ-PP ^b | 2.4903 | 186.3 | 50.90 | awCVSZ-PP | 2.4786 | 190.1 | 52.61 |
| | | CBS(aQ5) ^b | 2.4876 | 186.9 | 51.15 | CBS(awQ5) | 2.4758 | 190.7 | 52.89 |
| | CCSD(T)-F12b | aVDZ-PP | 2.4938 | 184.3 | 49.99 | awCVDZ-PP | 2.4804 | 188.9 | 51.84 |
| | | aVTZ-PP | 2.4895 | 186.5 | 50.89 | awCVTZ-PP | 2.4767 | 190.4 | 52.55 |
| | | aVQZ-PP | 2.4888 | 186.6 | 51.17 | awCVQZ-PP | 2.4774 | 190.3 | 52.68 |
| | | aVSZ-PP | 2.4880 | 186.9 | 51.30 | awCVSZ-PP | 2.4766 | 190.5 | 52.85 |
| | | experiment ^c | | | | | 2.4715 | 191.05 | 53.5 ± 0.1 |

^aResults with the awCVnZ-PP basis sets were obtained with all electrons correlated (except those replaced by the pseudopotential). OptRI auxiliary basis sets were used throughout. ^bRef 2. ^cRefs 40 and 41.

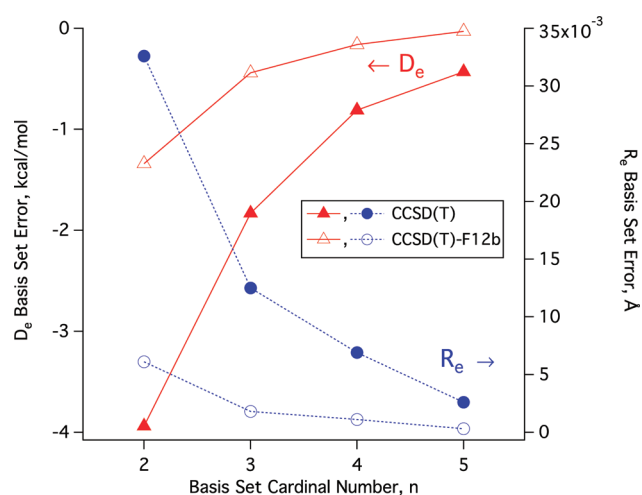


Figure 1. Convergence of the equilibrium dissociation energy (solid lines, in kcal mol^{-1}) and bond length (dotted lines, in Å) of Au_2 toward their estimated CBS limits ($51.33 \text{ kcal mol}^{-1}$ and 2.4877 Å , respectively) using both CCSD(T) and CCSD(T)-F12b with aug-cc-pVnZ-PP basis sets ($n = 2-5$). Only the valence electrons ($6s5d$) were correlated.

CCSD(T)/aVDZ-PP has basis set incompleteness errors of 0.0327 Å in R_e , 6.7 cm^{-1} in ω_e , and $3.76 \text{ kcal mol}^{-1}$ in D_e . Relative to the same CBS(aQ5) estimates, the CCSD(T)-F12b/aVDZ-PP

spectroscopic parameters have basis set incompleteness errors of just 0.0062 Å in R_e , 2.6 cm^{-1} in ω_e , and $1.16 \text{ kcal mol}^{-1}$ in D_e . Significantly, this indicates that meaningful results may now be accessible for much larger transition metal complexes, where aVDZ-PP is perhaps the only feasible basis set. It should be noted here that, as shown in Table SIV of the Supporting Information and in contrast to Cu_2 , the use of the larger geminal exponent of 1.4 slightly degrades the accuracy of the aVDZ-PP D_e values of both Ag_2 and Au_2 .

The results of calculations on the group 11 dimers where all of the electrons were correlated display very similar trends to CCSD(T)-F12b/the valence-only calculations—DZ F12b results that are typically within a couple of mÅ for R_e , around 1 cm^{-1} for ω_e , and within $0.5 \text{ kcal mol}^{-1}$ for D_e of the conventional QZ results. Explicitly correlated TZ results are generally very comparable in accuracy to the conventional SZ values and close to the conventional CBS limits. It is noteworthy that the explicitly correlated methods perform slightly worse for the Ag_2 dimer (compared to Cu_2 and Au_2), but these results still represent a significant improvement relative to the conventional cases.

The overall effects of correlating the $(n-1)$ s and p electrons on R_e , ω_e and D_e for the coinage metal dimers are summarized in Table SII in the Supporting Information. The core–valence effect is defined in this case as the difference in the value from the all-electrons correlated calculations and the equivalent result from the frozen-core calculation (employing

Table 6. Calculated spectroscopic constants for the $X^1\Sigma^+$ states of CuF, AgF, and AuF^a

| system | method | basis set | R_e (Å) | ω_e (cm ⁻¹) | D_e (kcal mol ⁻¹) | basis set | R_e (Å) | ω_e (cm ⁻¹) | D_e (kcal mol ⁻¹) |
|--------|--------------|-------------------------|-----------|--------------------------------|---------------------------------|-----------|-----------|--------------------------------|---------------------------------|
| CuF | CCSD(T) | aVDZ-PP | 1.7619 | 598.4 | 94.77 | awCVDZ-PP | 1.7624 | 594.3 | 93.93 |
| | | aVTZ-PP | 1.7464 | 613.7 | 96.92 | awCVTZ-PP | 1.7477 | 612.8 | 96.16 |
| | | aVQZ-PP | 1.7428 | 619.0 | 98.36 | awCVQZ-PP | 1.7454 | 617.0 | 97.47 |
| | | aVSZ-PP | 1.7420 | 619.4 | 98.67 | awCVSZ-PP | 1.7444 | 617.6 | 97.85 |
| | | CBS(aQ5) | 1.7415 | 619.5 | 99.02 | CBS(awQ5) | 1.7437 | 618.2 | 98.31 |
| | CCSD(T)-F12b | aVDZ-PP | 1.7418 | 618.1 | 98.54 | awCVDZ-PP | 1.7449 | 614.0 | 100.39 |
| | | aVTZ-PP | 1.7420 | 619.6 | 98.70 | awCVTZ-PP | 1.7447 | 617.3 | 98.41 |
| | | aVQZ-PP | 1.7413 | 620.6 | 99.01 | awCVQZ-PP | 1.7442 | 618.3 | 98.31 |
| | | aVSZ-PP | 1.7412 | 620.5 | 99.00 | awCVSZ-PP | 1.7441 | 618.3 | 98.32 |
| | | experiment ^b | | | | | 1.7449 | | 103.3 ± 1.0 |
| AgF | CCSD(T) | aVDZ-PP | 2.0101 | 501.2 | 77.13 | awCVDZ-PP | 1.9973 | 509.1 | 76.80 |
| | | aVTZ-PP | 1.9923 | 505.5 | 79.44 | awCVTZ-PP | 1.9823 | 512.2 | 78.91 |
| | | aVQZ-PP | 1.9885 | 510.0 | 80.87 | awCVQZ-PP | 1.9798 | 515.5 | 80.30 |
| | | aVSZ-PP | 1.9870 | 510.3 | 81.22 | awCVSZ-PP | 1.9789 | 515.9 | 80.67 |
| | | CBS(aQ5) | 1.9861 | 510.5 | 81.61 | CBS(awQ5) | 1.9783 | 516.3 | 81.13 |
| | CCSD(T)-F12b | aVDZ-PP | 1.9864 | 511.9 | 80.63 | awCVDZ-PP | 1.9788 | 516.9 | 82.64 |
| | | aVTZ-PP | 1.9859 | 511.7 | 81.18 | awCVTZ-PP | 1.9782 | 516.9 | 81.14 |
| | | aVQZ-PP | 1.9856 | 512.1 | 81.58 | awCVQZ-PP | 1.9780 | 517.0 | 81.15 |
| | | aVSZ-PP | 1.9857 | 511.7 | 81.57 | awCVSZ-PP | 1.9781 | 516.9 | 81.17 |
| | | experiment ^b | | | | | 1.9830 | | 82.6 ± 1.0 |
| AuF | CCSD(T) | aVDZ-PP | 1.9664 | 532.6 | 63.74 | awCVDZ-PP | 1.9503 | 545.5 | 64.91 |
| | | aVTZ-PP | 1.9420 | 541.4 | 66.80 | awCVTZ-PP | 1.9292 | 553.5 | 67.56 |
| | | aVQZ-PP | 1.9380 | 545.7 | 68.01 | awCVQZ-PP | 1.9267 | 556.2 | 68.54 |
| | | aVSZ-PP | 1.9361 | 546.8 | 68.39 | awCVSZ-PP | 1.9261 | 556.6 | 68.80 |
| | | CBS(aQ5) | 1.9351 | 547.9 | 68.80 | CBS(awQ5) | 1.9258 | 557.2 | 69.16 |
| | CCSD(T)-F12b | aVDZ-PP | 1.9360 | 545.4 | 67.71 | awCVDZ-PP | 1.9261 | 554.8 | 70.60 |
| | | aVTZ-PP | 1.9354 | 547.5 | 68.32 | awCVTZ-PP | 1.9257 | 556.6 | 69.21 |
| | | aVQZ-PP | 1.9351 | 547.7 | 68.67 | awCVQZ-PP | 1.9258 | 556.8 | 69.13 |
| | | aVSZ-PP | 1.9350 | 547.7 | 68.71 | awCVSZ-PP | 1.9257 | 556.7 | 69.19 |
| | | experiment ^c | | | | | 1.9184 | 563.7 | 69.4 |

^aResults with the awCVnZ-PP basis sets were obtained with all electrons on the group 11 element correlated (except those replaced by the pseudopotential). Explicitly correlated calculations used the cc-pVnZ-F12 basis sets for fluorine ($n = 4$ was used in combination with the $n = 5$ basis set on the transition metal), while conventional calculations utilized the aug-cc-pVnZ basis sets on F. OptRI auxiliary basis sets were used throughout. ^bSpectroscopic constants from ref 42 and D_0 values taken from ref 43 with adjustments for zero-point energies using the present work and with spin-orbit effects from the F atom removed.⁴⁴ ^cFrom the microwave work of ref 45.

the awCVnZ basis sets for both sets of calculations). It can be seen that the effect is essentially negligible for the Cu₂ dimer; a reduction in equilibrium bond length of around 0.001 Å, an increase in harmonic frequency of around 1 cm⁻¹, and almost no change in the bond dissociation energy is observed, which has been previously noted for both pseudopotential and all-electron basis sets. The changes in the equivalent spectroscopic constants for Ag₂ and Au₂ are significantly larger. For the silver dimer (with the largest basis set), there is a shortening of R_e by 0.012 Å, an increase in ω_e of 4.4 cm⁻¹, and an increase in D_e of 0.9 kcal mol⁻¹. The core-valence correlation effect for the gold dimer is observed to be of the same magnitude, with a slightly larger increase in D_e of 1.5 kcal mol⁻¹, in very good agreement with the conventional CCSD(T) results of Peterson and Puzzarini.³⁸ It can also be seen from Table SII that the core-valence effect converges very rapidly with basis set when explicitly correlated methods are employed, and unless very high accuracy results are required, it should be sufficient to evaluate the core-valence effect with the awCVDZ-PP basis set at the CCSD(T)-F12b level of theory.

Table 6 presents spectroscopic parameters for CuF, AgF, and AuF, evaluated both with the CCSD(T)-F12b method and with conventional CCSD(T). Once again, it can be seen that explicitly correlated TZ calculations produce spectroscopic

parameters comparable with conventional SZ values, which are close to the estimated CBS limits. The improved basis set convergence is particularly evident for the dissociation energies, especially when the awCVnZ-PP sets are used and the outer-core electrons are correlated. Further increasing the quality of the basis set typically leads to values that establish new reference data for the monofluorides, particularly for AgF and AuF. As mentioned above, the explicitly correlated calculations employed the cc-pVnZ-F12 ($n = D, T, Q$) basis sets on fluorine, and hence the cc-pVQZ-F12 basis sets were utilized in combination with both aVQZ-PP and aVSZ-PP on the coinage metals. As shown in Table 6, increasing the basis set on the coinage metal from QZ to SZ has a negligible effect on the values of R_e , ω_e , and D_e . The spectroscopic parameters for AuF from conventional CCSD(T) shown in Table 6 are consistent with those of Puzzarini and Peterson,³⁸ but the calculations were repeated in this work so that the same basis set extrapolation formula could be used for all of the coinage metal monofluorides.

Calculated equilibrium bond lengths and atomization energies (ΣD_e) for the coinage metal difluorides are shown in Table 7 and exhibit very similar trends as observed for the diatomics. Explicitly correlated calculations at the DZ level produce results that are close to the accuracy previously observed from the conventional method with QZ basis sets. Increasing the basis set to

Table 7. Calculated Equilibrium Bond Lengths and Atomization Energies for $X^1\Sigma_g^+$ CuF₂, AgF₂, and AuF₂^a

| system | method | basis set | R_e (Å) | ΣD_e (kcal mol ⁻¹) | basis set | R_e (Å) | ΣD_e (kcal mol ⁻¹) |
|------------------|--------------|-------------------------|-----------|--|-----------|-----------|--|
| CuF ₂ | CCSD(T) | aVDZ-PP | 1.7283 | 180.27 | awCVDZ-PP | 1.7275 | 179.21 |
| | | aVTZ-PP | 1.7161 | 184.69 | awCVTZ-PP | 1.7164 | 183.42 |
| | | aVQZ-PP | 1.7132 | 186.84 | awCVQZ-PP | 1.7137 | 185.24 |
| | | aVSZ-PP | 1.7122 | 187.34 | awCVSZ-PP | 1.7124 | 185.68 |
| | | CBS(aQ5) | 1.7114 | 187.82 | CBS(awQ5) | 1.7113 | 186.21 |
| | CCSD(T)-F12b | aVDZ-PP | 1.7113 | 188.71 | awCVDZ-PP | 1.7115 | 191.96 |
| | | aVTZ-PP | 1.7118 | 187.65 | awCVTZ-PP | 1.7120 | 186.71 |
| | | aVQZ-PP | 1.7113 | 187.96 | awCVQZ-PP | 1.7115 | 186.34 |
| | | aVSZ-PP | 1.7112 | 187.84 | awCVSZ-PP | 1.7115 | 186.30 |
| | | experiment ^b | | | | 1.700(14) | 186.5 ± 1.3 |
| AgF ₂ | CCSD(T) | aVDZ-PP | 1.9103 | 115.76 | awCVDZ-PP | 1.9032 | 119.59 |
| | | aVTZ-PP | 1.8919 | 120.79 | awCVTZ-PP | 1.8877 | 123.95 |
| | | aVQZ-PP | 1.8884 | 122.97 | awCVQZ-PP | 1.8851 | 125.76 |
| | | aVSZ-PP | 1.8867 | 123.51 | awCVSZ-PP | 1.8839 | 126.06 |
| | | CBS(aQ5) | 1.8856 | 124.04 | CBS(awQ5) | 1.8830 | 126.46 |
| | CCSD(T)-F12b | aVDZ-PP | 1.8873 | 123.03 | awCVDZ-PP | 1.8838 | 130.57 |
| | | aVTZ-PP | 1.8863 | 123.58 | awCVTZ-PP | 1.8832 | 126.95 |
| | | aVQZ-PP | 1.8859 | 124.13 | awCVQZ-PP | 1.8829 | 126.67 |
| | | aVSZ-PP | 1.8857 | 123.99 | awCVSZ-PP | 1.8829 | 126.63 |
| | | | | | | | |
| AuF ₂ | CCSD(T) | aVDZ-PP | 1.9279 | 116.74 | awCVDZ-PP | 1.9235 | 120.87 |
| | | aVTZ-PP | 1.9078 | 122.93 | awCVTZ-PP | 1.9047 | 126.11 |
| | | aVQZ-PP | 1.9038 | 125.10 | awCVQZ-PP | 1.9013 | 127.61 |
| | | aVSZ-PP | 1.9020 | 125.78 | awCVSZ-PP | 1.8999 | 127.96 |
| | | CBS(aQ5) | 1.9008 | 126.46 | CBS(awQ5) | 1.8986 | 128.45 |
| | CCSD(T)-F12b | aVDZ-PP | 1.9011 | 124.88 | awCVDZ-PP | 1.8985 | 132.28 |
| | | aVTZ-PP | 1.9013 | 125.67 | awCVTZ-PP | 1.8990 | 128.79 |
| | | aVQZ-PP | 1.9009 | 126.25 | awCVQZ-PP | 1.8988 | 128.43 |
| | | aVSZ-PP | 1.9008 | 126.30 | awCVSZ-PP | 1.8986 | 128.49 |
| | | | | | | | |

^aResults with the awCVnZ-PP basis sets were obtained with all electrons on the group 11 element correlated (except those replaced by the pseudopotential). Explicitly correlated calculations used the cc-pVnZ-F12 basis sets for fluorine ($n = 4$ was used in combination with the $n = 5$ basis set on the transition metal), while conventional calculations utilized the aug-cc-pVnZ basis sets on F. OptRI auxiliary basis sets were used throughout. ^bExperimental structure from ref 46. The equilibrium atomization energy was derived from the 298 K heat of formation of ref 47. Spin-orbit effects from the latter have been removed, see ref 48.

TZ quality produces spectroscopic parameters that are close to conventional SZ and estimates of the CBS limit. Only if the highest accuracy is desired should it be necessary to increase the basis set size to QZ or 5Z when explicitly correlated methods are employed for these molecules.

The effects of correlating the outer-core electrons on the transition metal element within the coinage metal monofluorides and difluorides are presented in Tables SII and SIII in the Supporting Information, respectively. In all cases, the 1s electrons on fluorine are held frozen in the correlation treatment. The F12b core–valence effect is relatively insensitive to basis set size, with almost negligible differences between DZ and 5Z data. Given the very small core–valence correlation effect for the copper dimer, it is perhaps surprising to find that CuF has a significantly larger core–valence effect, but of course the oxidation state is quite different in the latter case. The change in D_e is approximately 1 kcal mol⁻¹ and hence cannot be neglected if chemical accuracy is the goal.

The R_e , ω_e , and D_e for the group 12 fluorides (ZnF, CdF, and HgF) are presented in Table 8. The same trends are observed as in the analogous coinage metal molecules; explicitly correlated calculations yield results equivalent to about $(n + 2)$ Z in conventional calculations, and the improvement from employing QZ or 5Z basis sets is small. It can be noted however that for ZnF and CdF, the bond lengths obtained at the CCSD(T)-F12b/aVDZ level of theory are shorter than those obtained at

the TZ level. As shown in Table SVII, however, this also seems to be due to the use of the larger geminal exponent. For completeness, the effects of correlating the remaining electrons on the group 12 elements are listed in Table SII in the Supporting Information. Again, the core correlation effects converge rapidly with basis set for the F12b cases.

V. CONCLUSIONS

New auxiliary basis sets for use in the RI approximation within explicitly correlated calculations have been developed for the coinage metal (Cu, Ag, Au) and group 12 elements (Zn, Cd, Hg). These optimized ABSs (OptRI) are specifically matched to the standard aug-cc-pVnZ-PP orbital basis sets for valence-only correlation and the aug-cc-pwCVnZ-PP orbital basis sets for core–valence correlation. As the OptRI sets were developed within the CABS framework, where the ABS is combined with the underlying OBS, they are compact and ensure that no functions are deleted within the procedure, meaning that smooth potential energy surfaces can be obtained. The ABSs were benchmarked in the first F12 calculations of equilibrium geometries, harmonic vibrational frequencies, and atomization energies for coinage metal homonuclear dimers, coinage metal and group 12 monofluorides, and coinage metal difluorides. The results of these CCSD(T)-F12b calculations display very rapid convergence with respect to the basis set when compared with the results of conventional CCSD(T) calculations. Chemical accuracy is attained

Table 8. Calculated Spectroscopic Constants for the $X^1\Sigma^+$ States of ZnF, CdF, and HgF^a

| system | method | basis set | R_e (Å) | ω_e (cm ⁻¹) | D_e (kcal mol ⁻¹) | basis set | R_e (Å) | ω_e (cm ⁻¹) | D_e (kcal mol ⁻¹) |
|--------|--------------|-------------------------|-----------|--------------------------------|---------------------------------|-----------|-----------|--------------------------------|---------------------------------|
| ZnF | CCSD(T) | aVDZ-PP | 1.7825 | 619.0 | 65.93 | awCVDZ-PP | 1.7855 | 610.3 | 65.35 |
| | | aVTZ-PP | 1.7697 | 626.7 | 68.03 | awCVTZ-PP | 1.7705 | 627.5 | 67.43 |
| | | aVQZ-PP | 1.7653 | 632.6 | 69.66 | awCVQZ-PP | 1.7671 | 631.8 | 68.90 |
| | | aVSZ-PP | 1.7644 | 633.3 | 70.05 | awCVSZ-PP | 1.7660 | 632.5 | 69.33 |
| | | CBS(aQ5) | 1.7637 | 633.9 | 70.43 | CBS(awQ5) | 1.7650 | 633.1 | 69.83 |
| | CCSD(T)-F12b | aVDZ-PP | 1.7606 | 637.9 | 70.14 | awCVDZ-PP | 1.7645 | 635.4 | 71.86 |
| | | aVTZ-PP | 1.7638 | 634.7 | 70.03 | awCVTZ-PP | 1.7655 | 633.8 | 69.86 |
| | | aVQZ-PP | 1.7633 | 634.9 | 70.39 | awCVQZ-PP | 1.7650 | 633.9 | 69.79 |
| | | aVSZ-PP | 1.7633 | 634.0 | 70.37 | awCVSZ-PP | 1.7651 | 633.7 | 69.81 |
| | | experiment ^b | | | | | 1.7677 | 631 | 72.0 |
| CdF | CCSD(T) | aVDZ-PP | 1.9980 | 527.3 | 55.17 | awCVDZ-PP | 1.9950 | 525.4 | 54.31 |
| | | aVTZ-PP | 1.9851 | 529.7 | 57.41 | awCVTZ-PP | 1.9816 | 530.8 | 56.31 |
| | | aVQZ-PP | 1.9809 | 534.4 | 58.91 | awCVQZ-PP | 1.9780 | 535.3 | 57.80 |
| | | aVSZ-PP | 1.9795 | 534.9 | 59.27 | awCVSZ-PP | 1.9768 | 535.9 | 58.18 |
| | | CBS(aQ5) | 1.9785 | 535.4 | 59.64 | CBS(awQ5) | 1.9758 | 536.5 | 58.64 |
| | CCSD(T)-F12b | aVDZ-PP | 1.9749 | 539.2 | 59.05 | awCVDZ-PP | 1.9746 | 538.9 | 60.34 |
| | | aVTZ-PP | 1.9779 | 536.8 | 59.16 | awCVTZ-PP | 1.9756 | 537.4 | 58.60 |
| | | aVQZ-PP | 1.9778 | 536.8 | 59.62 | awCVQZ-PP | 1.9755 | 537.6 | 58.64 |
| | | aVSZ-PP | 1.9780 | 536.2 | 59.59 | awCVSZ-PP | 1.9756 | 537.3 | 58.66 |
| | | aVDZ-PP | 2.0527 | 469.6 | 27.73 | awCVDZ-PP | 2.0453 | 473.4 | 27.37 |
| HgF | CCSD(T) | aVTZ-PP | 2.0334 | 477.8 | 30.10 | awCVTZ-PP | 2.0271 | 480.7 | 29.44 |
| | | aVQZ-PP | 2.0286 | 483.1 | 31.20 | awCVQZ-PP | 2.0232 | 484.5 | 30.46 |
| | | aVSZ-PP | 2.0268 | 484.1 | 31.51 | awCVSZ-PP | 2.0217 | 486.2 | 30.78 |
| | | CBS(aQ5) | 2.0253 | 485.2 | 31.86 | CBS(awQ5) | 2.0204 | 487.9 | 31.20 |
| | | aVDZ-PP | 2.0251 | 483.1 | 31.26 | awCVDZ-PP | 2.0206 | 486.7 | 32.95 |
| | CCSD(T)-F12b | aVTZ-PP | 2.0253 | 485.2 | 31.47 | awCVTZ-PP | 2.0210 | 486.4 | 31.21 |
| | | aVQZ-PP | 2.0253 | 485.2 | 31.79 | awCVQZ-PP | 2.0209 | 486.7 | 31.15 |
| | | aVSZ-PP | 2.0254 | 484.9 | 31.81 | awCVSZ-PP | 2.0209 | 486.6 | 31.21 |

^aResults with the awCVnZ-PP basis sets were obtained with all electrons on the group 12 element correlated (except those replaced by the pseudopotential). Explicitly correlated calculations used the cc-pVnZ-F12 basis sets for fluorine ($n = 4$ was used in combination with the $n = 5$ basis set on the transition metal), while conventional calculations utilized the aug-cc-pVnZ basis sets on F. OptRI auxiliary basis sets were used throughout. ^bFrom the microwave study of ref 49.

with triple- ζ quality basis sets, while double- ζ results typically produce values comparable to those from the conventional method with quadruple- ζ basis sets. It is noted that when using explicitly correlated methods the core correlation effects are close to being converged with only a double- ζ quality basis set for all of the molecules considered in this investigation. Some sensitivity to the choice of the geminal exponent β was also observed, and larger values (~ 1.4) compared to those normally used for main group elements (~ 1.0) seem to be preferred in most cases.

With the development of appropriate ABSs for use in the RI, it has been demonstrated that explicitly correlated methods are capable of producing greatly enhanced convergence with respect to basis set for small transition metal compounds. With this route to high accuracy results at a reduced computational cost (due to using much smaller basis sets), it can be envisaged that wave function based methods may be more routinely used in a realm that has typically been the reserve of density functional theory. However, elements that occur earlier in the d-block of the periodic table are typically found in multiple spin states and their complexes are not easily described with a single Slater determinant. The development of compact RI ABSs for the remaining transition metal elements will require the use of multireference methods, such as CASPT2-F12 or MRCI-F12,^{7,39} in order to develop ABSs free of significant bias toward a single state. Investigations in this direction are currently underway. It is also of interest to determine if even better basis set convergence can be achieved for the transition metals by

optimizing new orbital basis sets specifically for explicit correlation, cc-pVnZ-F12-PP, as has been done for lighter elements. This will also be the subject of a future investigation.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The auxiliary basis sets developed in this work can be found in the Supporting Information together with Table SI through SVII, which contain additional results regarding core correlation for the homonuclear diatomics and fluorides and frozen-core spectroscopic properties obtained with alternative values of the geminal exponent β . This information is available free of charge via the Internet at <http://pubs.acs.org/>. The basis sets will also be made available for electronic download from one of the authors' Web site (<http://tyr0.chem.wsu.edu/~kipeters/basis.html>).

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Notes

The authors declare no competing financial interest.

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