Article:

Hill, J.G. orcid.org/0000-0002-6457-5837 and Shaw, R.A. (2021) Correlation consistent basis sets for explicitly correlated wavefunctions : pseudopotential-based basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements. Journal of Chemical Physics, 155 (17). 174113. ISSN 0021-9606

https://doi.org/10.1063/5.0070638

The Journal of Chemical Physics

Correlation consistent basis sets for explicitly correlated wavefunctions: Pseudopotential-based basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements

Cite as: J. Chem. Phys. **155**, 174113 (2021); https://doi.org/10.1063/5.0070638
Submitted: 08 September 2021 • Accepted: 15 October 2021 • Published Online: 02 November 2021

J. Grant Hill and Robert A. Shaw

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

Correlation consistent basis sets for explicitly correlated wavefunctions: Pseudopotential-based basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements

Cite as: J. Chem. Phys. **155**, 174113 (2021); doi: 10.1063/5.0070638
Submitted: 8 September 2021 • **Accepted:** 15 October 2021 •
Published Online: 2 November 2021

View Online Export Citation CrossMark

J. Grant Hill[a) and **Robert A. Shaw**

AFFILIATIONS

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom

[a)] **Author to whom correspondence should be addressed:** grant.hill@sheffield.ac.uk

ABSTRACT

New correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements have been developed specifically for use in explicitly correlated F12 calculations. This includes orbital basis sets for valence only (cc-pV*n*Z-PP-F12, *n* = D, T, Q) and outer core–valence (cc-pCV*n*Z-PP-F12) correlation, along with both of these augmented with additional high angular momentum diffuse functions. Matching auxiliary basis sets required for density fitting and resolution-of-the-identity approaches to conventional and F12 integrals have also been optimized. All of the basis sets are to be used in conjunction with small-core relativistic pseudopotentials [Figgen *et al.*, Chem. Phys. **311**, 227 (2005)]. The accuracy of the basis sets is determined through benchmark calculation at the explicitly correlated coupled-cluster level of theory for various properties of atoms and diatomic molecules. The convergence of the properties with respect to the basis set is dramatically improved compared to conventional coupled-cluster calculations, with cc-pVTZ-PP-F12 results close to conventional estimates of the complete basis set limit. The patterns of convergence are also greatly improved compared to those observed from the use of conventional correlation consistent basis sets in F12 calculations.

I. INTRODUCTION

The development of practical explicitly correlated methods in electronic structure theory has meant that accurate energies, structures, and properties of small-to medium-sized molecules can be obtained at a significantly reduced computational cost. Previously, their slow convergence with respect to the one-particle basis set used to describe atomic/molecular orbitals meant that large basis sets needed to be used, often in conjunction with extrapolation procedures to estimate a complete basis set (CBS) limit.[1–3] The history and development of explicitly correlated methods has been reviewed,[4–7] and only the briefest of introductions is given here. The so-called F12 explicitly correlated methods include one or more non-linear correlation factors, such as $e^{-\gamma r_{12}}$ (where γ is the geminal Slater exponent and r_{12} is the inter-electronic distance), into the wavefunction. This greatly accelerated the convergence with respect to basis set in methods such as explicitly correlated Møller–Plesset perturbation theory (MP2-F12),[8] explicitly correlated coupled cluster singles, doubles, and perturbative triples [CCSD(T)-F12*x* and CCSD(T)(F12)],[9–12] and explicitly correlated internal contracted multi-reference configuration interaction (MRCI-F12).[13]

While standard one-particle basis sets, such as the correlation consistent family,[14] can be used in explicitly correlated methods, it has been shown that Gaussian basis sets developed specifically for use in F12 approaches offer a number of advantages. This has led to the design and optimization of cc-pV*n*Z-F12 basis sets for the elements H–Ar[15–17] and cc-pV*n*Z-PP-F12 basis sets paired to pseudopotentials (PP) for the post-d main group elements Ga–Rn.[18] For lighter elements, these basis sets have also been augmented with additional core-correlating functions to form the cc-pCV*n*Z-F12 sets,[19] which lead to rapid convergence in the effect of core correlation on spectroscopic properties of small molecules. In the present work, new correlation consistent basis sets designed for use in F12 calculations, denoted cc-pV*n*Z-PP-F12 and cc-pCV*n*Z-PP-F12, have been developed for the group 11 and 12 elements. These basis sets are paired to the small-core relativistic PPs of Figgen *et al.*[20] and are derived from the standard diffuse augmented aug-cc-pV*n*Z-PP sets of Peterson and Puzzarini.[21] New auxiliary basis sets matched to these orbital basis sets have also been determined for use in the density fitting of the Fock and exchange integrals (JKFIT) and the density fitting of the remaining two-electron integrals (MP2FIT) and for use in the resolution-of-the-identity of the many-electron integrals from F12 theory (OptRI).

A previous investigation optimized OptRI auxiliary sets that enabled the use of standard aug-cc-pV*n*Z-PP orbital sets for groups 11 and 12 to be used in F12 calculations.[22] Subsequent CCSD(T)-F12b calculations on diatomic and triatomic molecules containing these elements demonstrated significantly improved performance, relative to the conventional method, for properties such as the dissociation energy and equilibrium geometry. However, in a number of cases, the convergence of these properties toward the complete basis set limit did not follow a regular pattern. One of the motivations for the present work is hence to determine if optimizing new orbital basis sets specifically for explicitly correlated methods lead to even better basis set convergence.

Details of the general computational methodology can be found in Sec. II, with the design, development, and optimization of the orbital and auxiliary basis sets in Sec. III. Benchmark calculations of both atomic and molecular properties, designed to validate the performance of the new sets, are reported and discussed in Sec. IV.

II. GENERAL COMPUTATIONAL DETAILS

The Molpro system of *ab initio* programs was used for the majority of this work,[23,24] with optimization and validation of MP2Fit auxiliary basis sets carried out with the TURBOMOLE program.[25,26] All of the atomic orbital basis sets developed in this work are paired with the small-core Dirac–Hartree–Fock adjusted pseudopotentials of the Stuttgart–Cologne variety,[20] replacing 10 electrons for Cu and Zn, 28 electrons for Ag and Cd, and 60 electrons for Au and Hg. Explicitly correlated calculations on molecules containing lighter elements used the cc-pV*n*Z-F12 basis sets of Peterson *et al.*,[15] and pure spherical harmonic angular momentum basis functions were used throughout. Explicitly correlated MP2 or coupled cluster calculations on open shell systems used restricted open-shell Hartree–Fock orbitals. Molecular benchmark calculations determined the dissociation energy (D_e), equilibrium bond length (r_e), and harmonic frequency (ω_e) by computing the energy of seven points distributed around the equilibrium geometry ($-0.3a_0 \le R - R_e \le +0.5a_0$) and fitting them with sixth-order polynomials before carrying out a Dunham analysis.[27] The weakly bound group 12 homonuclear dimers included a counterpoise correction for each energy point.[28]

III. BASIS SET DEVELOPMENT

A. Atomic orbital basis sets

The development of the atomic orbital basis sets specifically for use in explicitly correlated calculations closely follows previous work in this area.[15,16,18,19] Briefly, the optimizations of exponents used either BFGS or simplex algorithms and were carried out at the MP2-F12 level of theory using the 3C ansatz.[8] The geminal exponent was set to 1.4 a_0^{-1} for all exponent optimizations and energies were minimized for the electronic ground states of the neutral atoms. During the AO exponent optimizations, the auxiliary basis sets used were the def2-QZVPP/JKFit set for density fitting of the Fock and exchange matrices,[29] the aug-cc-pwCV5Z-PP/MP2Fit set for the density fitting of the remaining two-electron integrals (available in the TURBOMOLE basis set library), and an uncontracted (18s17p16d12f10g8h7i) even-tempered basis in the complementary auxiliary basis sets (CABS)[30] approach to the many-electron integrals that arise in F12 theory. The exponents of these large "reference" CABS sets are provided in the supplementary material.

The cc-pV*n*Z-F12 basis sets for other elements have used greater numbers of basis functions to describe the ground state occupied orbitals of the neutral atom than in the equivalent, conventional cc-pV*n*Z basis sets. This alleviates the problem noted for F12 calculations where the basis set incompleteness error in the Hartree Fock energy becomes larger than the error in the correlation energy.[15] The typical solution to this is to take the s and p parts of the basis set from the conventional aug-cc-pV($n+1$)Z basis, including both the contracted and correlating functions. A similar approach was also adopted here, with the s, p, and d exponents taken from the cc-pV($n+1$)Z-PP basis sets for use in the new cc-pV*n*Z-PP-F12 (n = D, T, Q) basis sets, along with the valence contraction coefficients to form a generally contracted [2s2p1d] core.

As a first step in determining the identity and number of correlating functions to include in each basis set, the incremental correlation energy lowering for the ^{2}S electronic state ($6s^1 5d^{10}$) of the neutral Au atom is displayed in Fig. 1. The correlation energies were obtained at the explicitly correlated internally contracted multireference configuration interaction (MRCI-F12)[13,31] level with a geminal Slater exponent of 1.4 a_0^{-1}. The f, g, h, and i correlating functions [Fig. 1(a)] were added in an even-tempered fashion to a base set of the contracted [6s6p5d] functions taken from the cc-pVQZ-PP basis set of Peterson and Puzzarini.[21] The energy increments were calculated in the standard correlation consistent manner; a single f function is added to the base spd functions and optimized, and then two to five f functions are optimized. This pattern then proceeds with g-type functions added to the resulting [6s6p5d5f] set and so-on. Figure 1(b) depicts the analogous results for s, p, and d correlation functions based on [2s6p5d3f2g1h], [6s1p5d3f2g1h], and [6s6p1d3f2g1h] base sets, respectively. The CABS singles correction was not included in the latter correlation energies.

Figure 1(a) shows that at first glance the MRCI-F12 results are similar to the standard configuration interaction results in previous correlation consistent basis set work. For example, the first f function recovers significantly more correlation energy than any other function considered and the second f function contributes roughly the same amount of energy as the first g type function. These groupings become much less obvious as the number of functions increases, with the increment due to the third f function being considerably less than that from the second g function or the first h function. The convergence of the s, p, and d correlation energy displayed in Fig. 1(b) is also far from smooth, with the second s function contributing a larger amount of correlation energy than the first, and a distinct kink

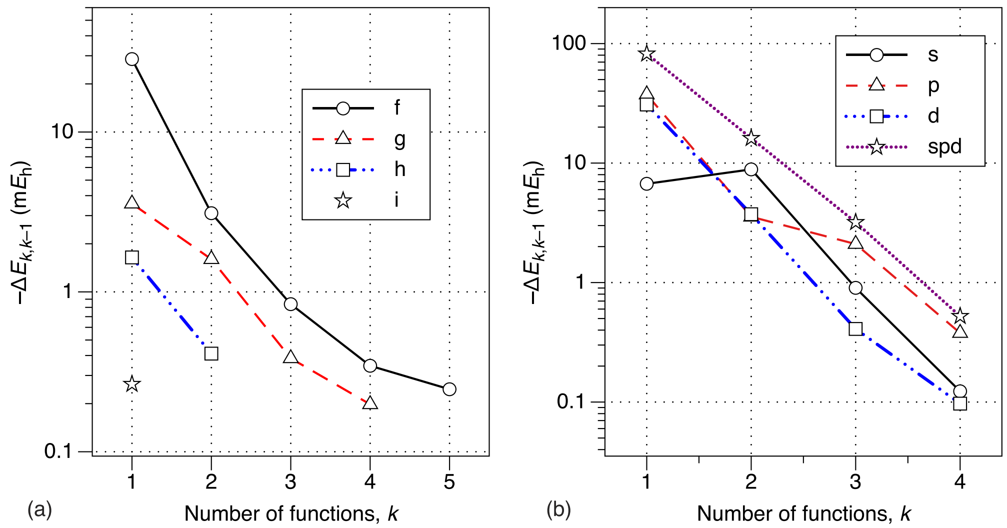

FIG. 1. Incremental contributions of the correlating functions to the MRCI-F12 correlation energy of the^{2}S electronic state of the Au atom, calculated for the (a) f, g, h, and i functions and (b) s, p, and d functions.

is visible between second and third p type functions. However, it is striking that when the correlation energy of the s, p, and d functions is summed (purple dotted line), a very smooth convergence pattern results. Comparing panels (a) and (b) of Fig. 1 suggests that the grouping of 2s2p2d functions makes a strong contribution to the correlation energy, approximately the same amount as a single f function. The contributions of the correlating functions detailed in Fig. 1 contrasts strongly with those observed from MP2-F12 calculations on the ground state of the Ne atom,[15] where it was obvious that the d type functions (the first with an angular momentum greater than that required to contain the electrons) make a very large contribution, with the third d function contributing more correlation energy than the first f function.

Correlation consistent basis sets for use in F12 calculations for lighter elements included at least two functions of each new angular momentum symmetry to provide a balanced description of both the HF and correlation energies. With this in mind and with the unclear fgh groupings in Fig. 1(a) and some preliminary testing on atomic and molecular properties, initial groupings were determined as 2f for DZ, 3f2g for TZ, and 4f3g2h for QZ. The exponents within these groupings were then optimized at the MP2-F12 level for the average total energy of the^{2}S and^{2}D electronic states for group 11 and the^{1}S state for group 12. The choice of using the MP2-F12 method for the final exponent optimization was made as in some cases numerical difficulties were encountered when using the MRCI-F12 method, leading to incredibly large correlation energies, and when using (U)CCSD-F12b, the exponents did not increase with Z as one would expect. For example, the exponents for Hg would be more diffuse than those for Au.

Conventional correlation consistent basis sets for transition metals have added spd correlating functions obtained from configuration interaction singles and doubles (CISD) atomic natural orbitals,[21,32] partly to ameliorate the well-established problems in correlating functions for pseudopotential-based basis sets.[33,34] A similar approach is followed here, with the spd correlating functions obtained from state-averaged MRCI-F12 ANOs, with two states (^{2}S and^{2}D) for group 11 and a single state (^{1}S) for group 12. Based on the analysis of incremental correlation energy above, this resulted in 2s2p2d correlating functions for DZ, 3s3p3d for TZ, and 4s4p4d for QZ. The outermost exponent was also uncontracted from the HF set for additional flexibility. The single augmenting s, p, and d diffuse functions from aug-cc-pV(n + 1)Z were also included in the cc-pVnZ-PP-F12 basis sets, continuing to follow the general prescription of the cc-pVnZ-F12 basis sets for lighter elements. The final composition of these basis sets is presented in Table I. A comparison of these basis sets with the conventional aug-cc-pVnZ-PP indicates that the basis sets developed in this work are larger by 1s1p1d, which follows the trend established by F12 sets for lighter elements.

TABLE I. Composition of the atomic orbital basis sets developed in this work for the group 11 and 12 elements.

Atomic orbital basis set	Composition
cc-pVDZ-PP-F12	[6s6p5d2f]
cc-pVTZ-PP-F12	[7s7p6d3f2g]
cc-pVQZ-PP-F12	[8s8p7d4f3g2h]
cc-pCVDZ-PP-F12	[7s7p6d3f]
cc-pCVTZ-PP-F12	[8s8p7d4f3g]
cc-pCVQZ-PP-F12	[9s9p8d5f4g3h]
aug-cc-pVDZ-PP-F12	[6s6p5d3f]
aug-cc-pVTZ-PP-F12	[7s7p6d4f3g]
aug-cc-pVQZ-PP-F12	[8s8p7d5f4g3h]

For the group 11 and 12 elements, the outer core $(m-1)$ sp electrons are usually excluded from the correlation treatment. However, conventional calculations aiming to recover the effects of core–valence correlation should use the weighted core–valence correlating cc-pwCV*n*Z-PP basis sets with the $(m-1)$ sp electrons correlated. Previous investigations into core–valence effects with explicitly correlated wave functions resulted in cc-pCV*n*Z-F12 basis sets for first and second row elements,[16,19] where the cc-pV*n*Z-F12 basis sets were augmented with a small number of tight-exponent core correlating functions. Following Ref. 19, an additional set of 1s1p1d functions were added to the cc-pV*n*Z-PP-F12 basis sets described above, with the exponents optimized for the change in correlation energy due to correlating the $(m-1)$ sp electrons at the MP2-F12 level. As in the conventional basis sets,[21,32] for the higher angular momentum functions (fgh), only the most diffuse function from cc-pV*n*Z-PP-F12 was retained and new sequences of functions optimized. The compositions in Table I show that the core–valence correlating sets have only one additional function in each angular momentum symmetry, relative to the valence-only correlating sets, for all zeta-levels. The core–valence correlating functions were determined for the ^{2}S electronic state of the group 11 elements and the ^{1}S state for group 12.

Initial testing of the cc-pV*n*Z-PP-F12 basis sets demonstrated that while these do contain diffuse s, p, and d functions, they did not provide an accurate description of electron affinities. Martin and co-workers previously noted poor basis set convergence for cc-pV*n*Z-F12 basis sets for anions of lighter elements,[35] and augmented these basis sets with diffuse, high-angular momentum functions to produce aug-cc-pV*n*Z-F12 sets.[36] In a similar fashion, the cc-pV*n*Z-PP-F12 sets developed in this work have been augmented with a single diffuse f function at DZ, 1f1g at TZ, and 1f1g1h at QZ, with full compositions given in Table I. As in the conventional cc-pV*n*Z-PP work, the exponents of these functions were obtained as even-tempered extensions of the most diffuse functions in the cc-pCV*n*Z-PP-F12 basis sets. The resulting exponents are then added to the cc-pV*n*Z-PP-F12 and cc-pCV*n*Z-PP-F12 sets to produce aug-cc-pV*n*Z-PP-F12 and aug-cc-pCV*n*Z-PP-F12 basis sets, respectively.

Figures 2–4 display the convergence of the CCSD correlation energy, with respect to basis set, in both conventional and CCSD-F12b calculations for the closed shell group 12 atoms Zn, Cd, and Hg. In conventional calculations, the aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-PP basis sets have been used and for brevity are abbreviated to aV*n*Z and awCV*n*Z, respectively. In F12 calculations, the basis sets developed in this work are abbreviated V*n*Z-F12, while the use of the conventional aug-cc-p(wC)V*n*Z-PP basis set in F12 calculations is denoted a(wC)V*n*Z(F12). For the latter series of basis sets, the previously developed OptRI auxiliary sets are used.[22] Estimated CBS limits are shown based upon conventional CCSD $(n+1)^{-3}$ extrapolations of the aug-cc-pwCV*n*Z-PP basis sets with $n = 4$ and 5.[37–39] The $n+1$ based extrapolation has been shown to provide better results for transition metal basis sets than the analogous extrapolation with just n,[39] but it is noted that $n+1$ is equivalent to $\ell_{\max}$ for d-block elements. Figure 2 shows the frozen-core correlation energy, where only the valence s and d electrons are correlated, and as expected, the F12 results are closer to the CBS estimates than the conventional calculations. Moreover, for both Cd and Hg, the F12 results with $n = 4$ or 5 results are lower in energy than the CBS estimate from conventional calculations. As the F12 correlation energies converge smoothly and rapidly, this demonstrates the slow convergence of conventional methods for these elements and suggests that F12 methods could be used to establish more reliable CBS estimates. In the case of Zn, the benefit of using F12 methods over conventional appears less striking, yet still beneficial; using the cc-pVDZ-PP-F12 basis set developed in this work produces a correlation energy that is somewhere between the conventional QZ and 5Z results or very close to the QZ result if the aug-cc-pwCV*n*Z-PP basis sets are used. Comparing the performance of the new sets with the performance of aug-cc-pV*n*Z-PP, both in F12 calculations, indicates that the correlation energy with the new sets is lower, although this becomes less pronounced as we move further down the group. Figures S1–S3 in the supplementary material plots only the F12

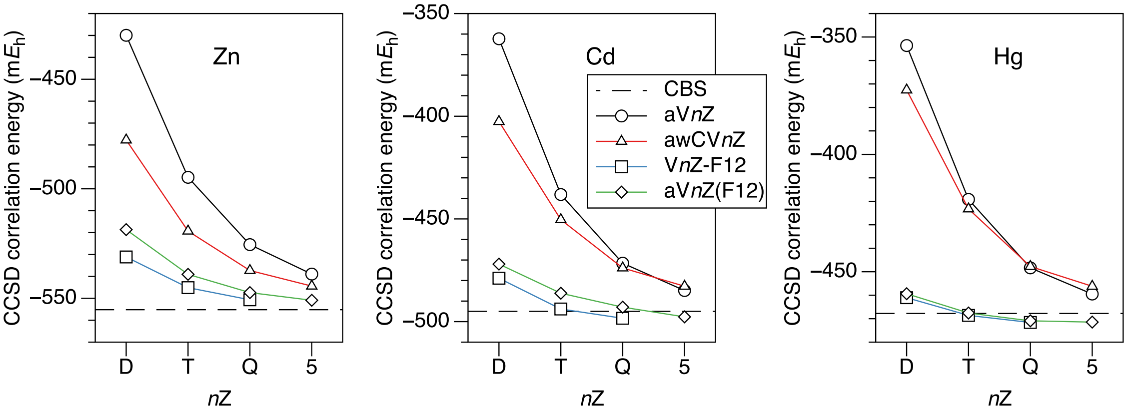

FIG. 2. Convergence of the valence CCSD correlation energies from conventional (aV*n*Z and awCV*n*Z) and explicitly correlated CCSD-F12b calculations [V*n*Z-F12 and aV*n*Z(F12)]. The estimated CBS limits are shown by dashed horizontal lines, which were obtained by $(n+1)^{-3}$ extrapolation of conventional aug-cc-pwCV*n*Z-PP correlation energies with $n = 4, 5$.

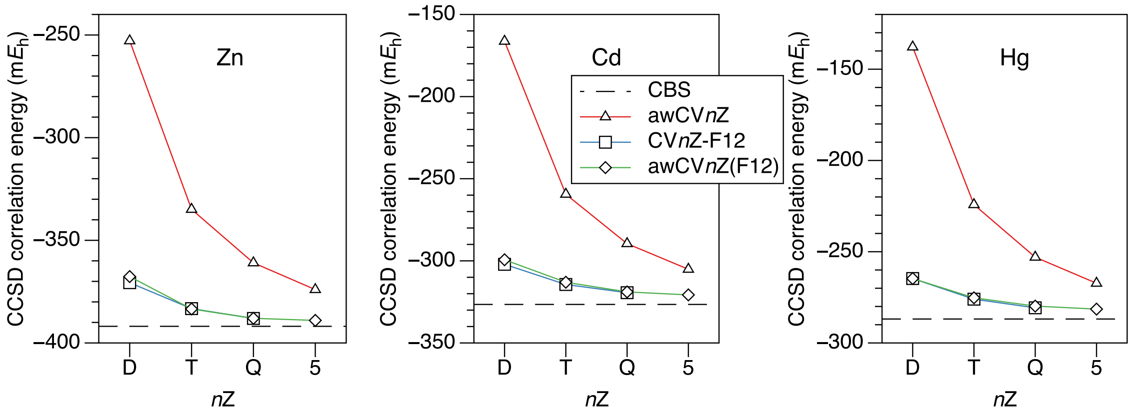

FIG. 3. Convergence of the CCSD ($m-1$)sp electron core–valence correlation energies from conventional (awCV*n*Z) and explicitly correlated CCSD-F12b calculations [CV*n*Z-F12 and awCV*n*Z(F12)]. The estimated CBS limits are shown by dashed horizontal lines, which were obtained by $(n+1)^{-3}$ extrapolation of conventional aug-cc-pwCV*n*Z-PP correlation energies with $n = 4, 5$.

correlation energies, and in the absence of the conventional results, the improvement in performance afforded by the new sets can be clearly seen.

Figures 3 and 4 show the convergence of the core–valence and core–core CCSD energies with respect to basis set, and it can be seen that the F12 calculations significantly accelerate the rate of convergence. Dramatically, even at the DZ level, the basis sets developed in this work are recovering almost the same conventional aug-cc-pwCV5Z-PP result, or even surpassing it. The convergence of the F12 energies with basis appears monotonic in all cases. Within the F12 framework, the basis sets developed in this work are slightly lower in energy than using the aug-cc-pwCV*n*Z-PP sets in F12 calculations, although the improvements in these absolute core correlation energies are modest compared to those for the valence correlation.

The size of the basis sets developed in this work is compared against the conventional correlation consistent basis sets for the group 11 and 12 elements in Table S1 in the supplementary material. As the new cc-pV*n*Z-PP-F12 basis sets contains the s, p, and d augmenting functions from the aug-cc-pV(*n*+1)Z-PP sets, the most appropriate comparison to make is in terms of the final contracted sizes of the cc-pV*n*Z-PP-F12 and aug-cc-pV*n*Z-PP sets. The new sets include one additional s, one p, and one d functions, for a total of nine extra contracted functions for each value of *n*. This minor increase is consistent with cc-pV*n*Z-F12 basis sets for first and second row elements, which contain one additional s and two p functions when compared to aug-cc-pV*n*Z.[15] Comparing the new cc-pCV*n*Z-PP-F12 core-correlating basis sets with aug-cc-pCV*n*Z-PP reveals that while the new DZ set contains an additional one s, one p, and one d functions, at the

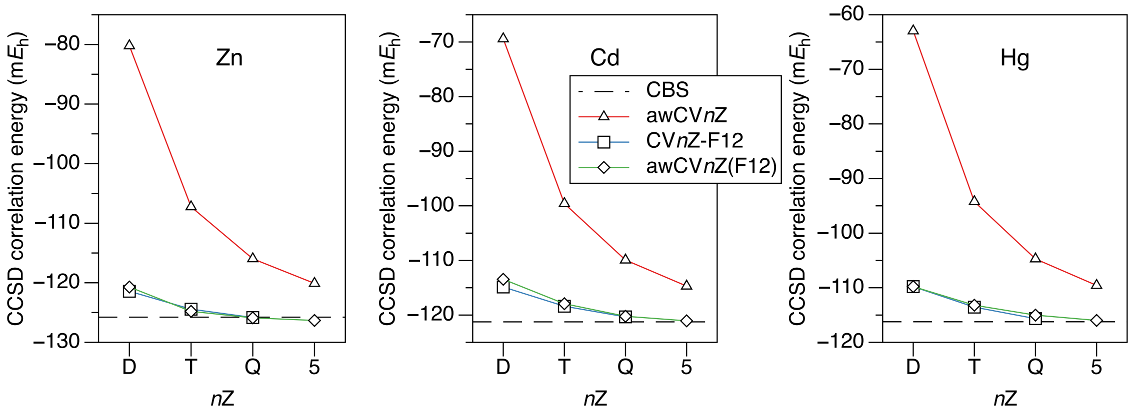

FIG. 4. Convergence of the CCSD ($m-1$)sp electron core–core correlation energies from conventional (awCV*n*Z) and explicitly correlated CCSD-F12b calculations [CV*n*Z-F12 and awCV*n*Z(F12)]. The estimated CBS limits are shown by dashed horizontal lines, which were obtained by $(n+1)^{-3}$ extrapolation of conventional aug-cc-pwCV*n*Z-PP correlation energies with $n = 4, 5$.

TZ and QZ levels, the total number of contracted functions is the same.

B. Density fitting auxiliary basis sets

Two auxiliary density fitting basis sets are typically required in explicitly correlated methods implemented in widely available electronic structure packages: an auxiliary basis for the density fitting of the Fock and exchange matrices (suffixed JKFIT) and a separate auxiliary basis for the density fitting of the remaining conventional two-electron integrals (MP2FIT). For JKFIT, it is standard practice to use the auxiliary basis matched to the aug-cc-pV*n*Z family of orbital basis, while MP2FIT is developed specifically for use with the cc-pV*n*Z-F12 basis. Both JKFIT and MP2FIT sets were developed as part of this work.

For the first of these, the JKFIT sets, the procedure previously used by Weigend was closely followed.[29,40,41] These are built as uncontracted functions optimized so as to minimize the error in the Hartree–Fock exchange energy as computed with and without the density fitting approximation. The objective function is thus

$$\delta_{\text{EX}} = \left|\text{Tr}\left\{\mathbf{P}^{\text{DF}}\mathbf{K}^{\text{DF}}\right\} - \text{Tr}\left\{\mathbf{P}^{\text{Full}}\mathbf{K}^{\text{Full}}\right\}\right|^2, \tag{1}$$

where **P** and **K** are the density matrix and exchange integrals, respectively, calculated either with density-fitted or full integrals. We fit only against the exchange integrals as it has been found previously that these errors dominate those due to fitting of the Coulomb integrals, meaning the so-called KFit sets are equally applicable as JFit sets. Optimizations are performed so as to reduce δ_{EX} on the mono-chloride of the atom. This is necessary because the HF exchange energy for the atom alone only depends on the occupied orbitals, and thus, higher angular momentum functions would not be optimized. Traditionally, the mono-hydride has been used for these optimizations because it is the smallest possible molecule system containing the atom. However, this resulted in overly diffuse exponents in the higher angular momentum shells, and errors could be significantly reduced by instead optimizing against the mono-chloride.

For each set, the starting point is a near-complete reference set of even-tempered functions for each angular momentum shell up to and including the highest angular momentum in the orbital basis plus a shell one angular momentum higher. For example, for the cc-pVDZ-PP-F12 orbital set for which the maximum angular momentum shell is of f-type, a g-type shell is also included in the auxiliary basis. From this large even-tempered basis, functions that change the objective function by less than a threshold of 10^{-7} E_{h} were systematically removed. The s- and p-functions are then optimized simultaneously, before being fixed, and then each subsequent angular momentum shell is optimized independently. At each stage, additional functions were removed if their impact on the objective was below the aforementioned threshold and the shell re-optimized. The resulting configurations for each JKFit basis can be found in Table S2 of the supplementary material. Each set contains roughly twice as many functions as the (contracted) orbital basis, which is in keeping with—in fact, slightly more compact than—previous results.[29]

TABLE II. Energy errors (μE_{h}) in the Hartree–Fock (ΔE_{HF}) and conventional MP2 correlation (ΔE_{MP2}) energies due to the use of density fitting of the Coulomb and exchange matrices. These were calculated using the JKFIT auxiliary basis sets developed in this work. The errors in the MP2 correlation energy were computed without density fitting of the transformed two-electron integrals. Estimated basis set incompleteness errors (BSIEs) for the HF energy from a large reference basis are also shown for comparison. Summary statistics are given across a test set comprising 36 molecules containing group 11 or 12 elements.

Atomic orbital basis set	Error type	MUE	σ	MAX
cc-pVDZ-PP-F12	BSIE	9628.09	5794.09	23 603.69
	ΔE_{HF}	729.77	306.07	1 377.79
	ΔE_{MP2}	149.19	83.50	318.50
cc-pVTZ-PP-F12	BSIE	1800.37	1188.39	4 878.16
	ΔE_{HF}	82.88	49.09	199.26
	ΔE_{MP2}	22.75	12.26	70.83
cc-pVQZ-PP-F12	BSIE	166.60	106.18	380.15
	ΔE_{HF}	20.38	13.60	61.74
	ΔE_{MP2}	11.45	3.70	21.29

Table II shows summary statistics for the errors in the density-fitted Hartree–Fock energy and the conventional MP2 correlation energy using the DF-HF density, for each of the JKFIT sets developed here, calculated over a set of 36 small molecules containing group 11 or 12 elements. The individual molecules are listed in the supplementary material, with the geometries either obtained from the test set of Weigend[41] or optimized using the same BP86/def-SVP level of theory.[42–44] For reference, we also show the basis set incompleteness error (BSIE) for the conventional HF energy, compared to results calculated in a large reference basis, namely, aug-cc-pV5Z(-PP). In each case, the mean unsigned error (MUE) and maximum absolute error (MAX) in the HF energy due to the use of density fitting is more than an order of magnitude smaller than the BSIE, and the error in the correlation energy is roughly five times smaller again. There is quite a wide standard deviation (σ) in the errors, but overall they remain significantly below the order-of-magnitude test suggested by Weigend.[40] Moreover, these errors are seen to reduce systematically with increasing cardinality of the basis while maintaining compactness of the auxiliary basis.

The design and optimization strategies for the MP2FIT auxiliary basis closely follows those developed for the cc-pV*n*Z-F12 basis sets for the elements H–Ar,[45] which built upon previous work on DF-MP2 auxiliary basis sets.[46,47] Briefly, the auxiliary basis sets comprise uncontracted primitives that were obtained from minimizing the functional

$$\delta_{\text{DF}} = -\frac{1}{4}\sum_{aibj}\frac{\left(\langle ab\|ij\rangle_{\text{DF}} - \langle ab\|ij\rangle\right)^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}, \tag{2}$$

where ϵ_x are Hartree–Fock orbital energies, i and j occupied orbitals, a and b virtual orbitals, and the two-electron repulsion integrals are denoted $\langle ab\|ij\rangle = (ai|bj) - (aj|bi)$. The density fitting error in the correlation energy is defined as $\Delta\text{DF} = |E^{\text{corr}}_{\text{MP2}} - E^{\text{corr}}_{\text{DF-MP2}}|$. The optimizations were performed using the analytical gradients within the RICC2 module in TURBOMOLE[48,49] under the guidelines that the ΔDF error for a given atom should be less than 1.0 μE_{h} per correlated electron and $\delta_{\text{DF}}/|E^{\text{corr}}_{\text{MP2}}|$ should be less than or equal to 10^{-8}.[45] All atoms were in their respective ground states, and initially, the auxiliary sets were optimized to specifically match the cc-pV*n*Z-PP-F12 orbital sets developed in this work, with only the valence electrons included in the correlation treatment. The composition of the resulting auxiliary basis sets is presented in Table S3 in the supplementary material, where it can be seen that at the QZ level, it was necessary to include more functions for Au and Hg than for the other group 11 and 12 elements. The reasons for this are unclear, but attempting to use fewer functions created both stability problems in the optimization and a significant reduction in accuracy. In all cases, the ratio of functions in the auxiliary basis set compared to the number of (contracted) functions in the orbital basis is less than the guideline maximum of six established in previous work on MP2FIT basis sets matched to F12 specific basis sets.[45]

Additional MP2FIT sets specifically matched to the core–valence correlating cc-pCV*n*Z-PP-F12 orbital sets were also optimized, with the $(m-1)$ sp electrons correlated. The cc-pV*n*Z-PP-F12/MP2FIT sets were taken as a starting point, with all exponents freely optimized and additional functions added until sufficient accuracy was reached. Both of these MP2FIT sets were also adapted for use with diffuse augmented orbital sets by adding a small number of additional small-exponent auxiliary functions, with all other exponents held fixed, resulting in the aug-cc-pV*n*Z-PP-F12/MP2FIT and aug-cc-pCV*n*Z-PP-F12/MP2FIT sets. The compositions of these sets are given in Table S3.

The performance of the MP2FIT auxiliary sets in molecular calculations has been validated by comparing the DF error in the conventional MP2 correlation energy with the MP2-F12 basis set incompleteness error using the same test set of 36 molecules as in the JKFIT work. To define the BSIE, estimates of the CBS correlation energy limit were obtained from (R)MP2-F12/3C(FIX) calculations carried out in Molpro, followed by a Schwenke-type extrapolation of the TZ and QZ correlation energies.[50,51] The cc-pV*n*Z-F12 basis set was used for lighter elements, along with the matching MP2FIT and OptRI auxiliary basis sets. It should be noted that the performance of this basis set extrapolation for heavier elements is not well tested, but it is used here simply to produce reasonable estimates of the BSIE rather than to establish benchmark-quality CBS limits. Separate CBS limits were obtained with the $(m-1)$ sp electrons correlated on the group 11 or 12 elements for benchmarking cc-pCV*n*Z-PP-F12 sets, while all other elements used the standard frozen core definition in all cases.

Table III presents the summary statistics for both the BSIE in the MP2-F12 correlation energy and ΔDF for the test set of molecules. A comparison of the statistics for BSIE and ΔDF indicates that for all basis sets, the error due to the density fitting is negligible relative to the basis set error in the correlation energy, even when an explicitly correlated method is used. Indeed, the DF error is three to four orders of magnitude smaller than the BSIE. It can be also seen that both ΔDF and the BSIE reduce as the basis set cardinal number is increased and that the errors when the outer-core electrons are correlated on the group 11 or 12 elements are approximately the same as the valence-only case.

TABLE III. Correlation energy errors (μE_h per correlated electron) due to the MP2-F12 basis set incompleteness error (BSIE) and conventional MP2 density fitting (ΔDF) using the MP2FIT auxiliary sets developed in this work. The test set comprises 36 molecules containing group 11 or 12 elements.

Atomic orbital basis set	Error type	MUE	σ	MAX
cc-pVDZ-PP-F12	BSIE	1593.69	374.56	2300.01
	ΔDF	0.34	0.21	0.76
cc-pVTZ-PP-F12	BSIE	457.43	101.94	663.50
	ΔDF	0.19	0.11	0.40
cc-pVQZ-PP-F12	BSIE	121.92	27.17	176.84
	ΔDF	0.08	0.06	0.21
cc-pCVDZ-PP-F12	BSIE	1320.12	222.64	1734.61
	ΔDF	0.23	0.16	0.58
cc-pCVTZ-PP-F12	BSIE	359.41	60.42	463.02
	ΔDF	0.14	0.07	0.29
cc-pCVQZ-PP-F12	BSIE	95.79	16.10	123.41
	ΔDF	0.06	0.04	0.16

C. Complementary auxiliary basis sets

The auxiliary basis sets required for the RI evaluation of the multi-electron F12 integrals were optimized using a similar methodology as the OptRI sets of Yousaf and Peterson.[52] Briefly, the auxiliary sets are intended for use within the complementary auxiliary basis set (CABS+) approach,[30] as implemented in Molpro, and are specifically matched to a particular atomic orbital basis set. This results in a compact and linearly independent CABS basis set where zero functions are deleted within the CABS procedure. The functions within the OptRI basis set are optimized for atoms by minimizing the value of δRI,

$$\delta\mathrm{RI} = \sum_{ij} \frac{V_{ij,ij}^{\mathrm{RI}} - V_{ij,ij}^{\mathrm{RI_{ref}}}}{V_{ij,ij}^{\mathrm{RI_{ref}}}} + \frac{B_{ij,ij}^{\mathrm{RI}} - B_{ij,ij}^{\mathrm{RI_{ref}}}}{B_{ij,ij}^{\mathrm{RI_{ref}}}}, \tag{3}$$

which involves the diagonal elements of the **V** and **B** matrices from MP2-F12 theory.[8] In this case, the reference matrices were computed using the large even-tempered sets described above, the 3C ansatz was used, and a geminal exponent of 1.4 a_0^{-1} was used throughout. In previous work on lighter elements, the OptRI basis sets have been augmented with a small number of s- and p-functions to obtain a greater CABS singles correction to the HF energy, with the resulting sets denoted OptRI+.[53] A similar approach was tested in the present investigation, but it was found that no significant increases in the CABS singles correction were obtained.

The compositions of the OptRI sets developed in this work can be found in Table S4 in the supplementary material, where it can be seen that the auxiliary sets are relatively compact, especially compared to MP2FIT. The cc-pCV*n*Z-PP-F12/OptRI sets possess slightly fewer functions than the analogous valence-only set, but this is to be expected as the total CABS + basis is formed from the union of the orbital basis and the functions from the OptRI set. In regard to an appropriate CABS set to use with the diffuse augmented orbital basis sets, initial testing has demonstrated that at the DZ and TZ level, the cc-p(C)V*n*Z-PP-F12/OptRI auxiliary sets combined with the aug-cc-p(C)V*n*Z-PP-F12 orbital sets produce only negligible changes in δRI and the total energy of the ground states of the atoms. However, at the QZ level, it was clear that some modifications would be required. In the valence-only case, the addition of

TABLE IV. RI errors (OptRI relative to the large reference ABS) per correlated electron in the MP2-F12/3C(FIX) correlation energies for a test of 36 molecules containing group 11 or 12 elements. All values are in μE_h.

Atomic orbital basis set	Error type	MUE	σ	MAX
cc-pVDZ-PP-F12	BSIE	1593.69	374.56	2300.01
	RI	28.46	9.31	50.65
cc-pVTZ-PP-F12	BSIE	457.43	101.94	663.50
	RI	3.32	3.20	10.37
cc-pVQZ-PP-F12	BSIE	121.92	27.17	176.84
	RI	0.81	0.55	1.96
cc-pCVDZ-PP-F12	BSIE	1320.12	222.64	1734.61
	RI	25.31	8.42	47.74
cc-pCVTZ-PP-F12	BSIE	359.41	60.42	463.02
	RI	3.56	1.69	7.95
cc-pCVQZ-PP-F12	BSIE	95.79	16.10	123.41
	RI	0.77	0.60	2.13

an extra h function and a re-optimization of all h exponents were sufficient in all cases except for Au, where re-optimization of the d, g, and i exponents, while holding all other exponents fixed, was also required. The QZ core–valence OptRI sets were also augmented with an additional h function, and the d, g, and i exponents were re-optimized for Ag, Cd, Au, and Hg. At this cc-pCVQZ-PP-F12 level, it was also necessary to include a single additional s function for Cd for the δRI error to be approximately the same as that for the other elements.

The errors in the MP2-F12/3C(FIX) correlation energy from using the OptRI sets developed in this work, relative to the reference RI set, were evaluated for the same set of test molecules as used in the density fitting auxiliary basis set work above, with the results presented in Table IV. The cc-pV*n*Z-F12 basis set was used for lighter elements, along with the matching MP2FIT and OptRI auxiliary basis sets. As in Table III, the energetic error from the use of the auxiliary basis sets developed in this work was compared to the BSIE for the orbital basis at the MP2-F12/3C(Fix) level. It can be seen that the errors from using the OptRI sets are roughly two orders of magnitude smaller than the MP2-F12 BSIE and that the error reduces as the basis set cardinal number is increased. The error per correlated electron also remains approximately equal for both the valence-only and outer-core–valence cases.

D. Choice of geminal exponent

The value of the geminal Slater exponent that produces the lowest correlation energy is known to depend upon the choice of orbital basis set, the explicitly correlated method chosen, and the atoms/molecules under consideration.[15,51,54] For lighter elements, typically a compromise value is chosen and used across methods and molecules, although larger geminal exponents are often used for larger basis sets. This choice becomes even more convoluted when core electrons are correlated as the optimal Slater exponent changes for the core–core, core–valence, or valence–valence pairs.[55] However, while a pair-specific geminal approach produces lower energies, often the change in the resulting properties is minor and a single value can be used for all pairs.[19,56] A previous investigation using explicitly correlated methods on molecules containing group 11 and 12 elements noted that larger values of the geminal exponent (around 1.4 a_0^{-1}) seemed to be preferred to those often used for main group elements (around 1.0 a_0^{-1}).[22] Herein, a more expansive test of the sensitivity of correlation energies to the choice of geminal exponent is undertaken.

Figure 5 shows the geminal exponent (γ) dependence of the valence-only, core–valence, and core–core MP2-F12 correlation energies for the near-equilibrium geometry of Cu_2, with analogous plots for Ag_2 and Au_2 provided in the supplementary material. The cc-pCVTZ-PP-F12 basis sets developed in this work, along with the matching auxiliary basis sets, are used throughout. To aid comparison, all plots span a range of 15 mE_h on the ordinate axis. For all three diatomic molecules, it can be seen that the dependence of the

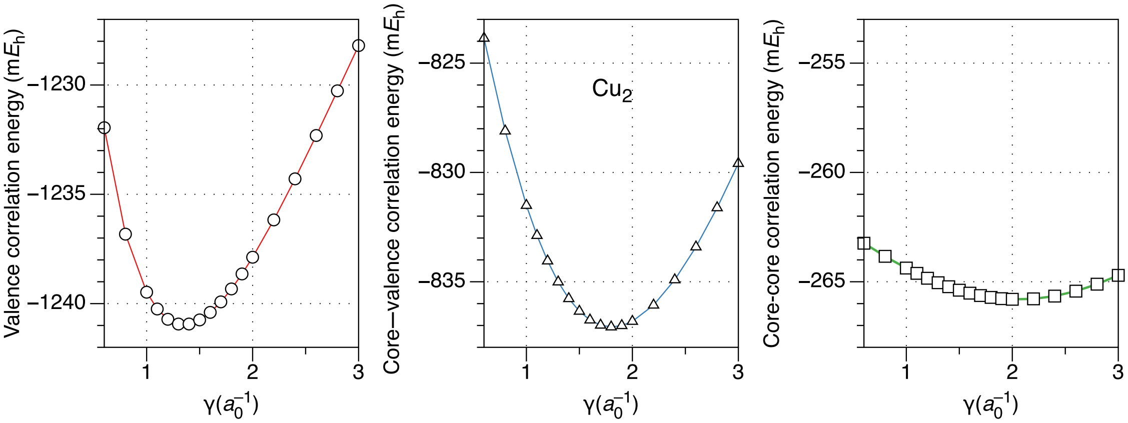

FIG. 5. Dependence of the valence, core–valence, and core–core MP2-F12/3C(Fix) correlation energies on the geminal exponent (γ). The cc-pCVTZ-PP-F12 basis was used, $r(Cu_2)$ = 2.2108 Å.

core–core contribution is significantly weaker than valence-only and core–valence, with the latter two having a roughly similar dependence. The core–core correlation energy is also smaller in magnitude; hence, the recommendation of a single value to use for group 11 and 12 elements will be based on valence-only and core–valence energies.

It is clear that a smaller value of γ is optimal for valence-only, with a slightly larger value favored for core–valence. It is also apparent that the dependence follows the trend $Cu_2 > Ag_2 > Au_2$, and the results with DZ and QZ basis sets (not shown) are very similar. Recommending a single value of γ to be used is thus somewhat challenging, although 1.4 a_0^{-1} appears to be a reasonable compromise value; for Cu_2, this is the optimal value for valence-only and close to optimal for core–valence. For Ag_2 and Au_2, this is relatively close to the minimum valence-only energy and provides essentially optimal energies for core–valence. Using two geminals with values of 1.0 a_0^{-1} and 1.4 a_0^{-1} for valence-only and core–valence, respectively, would lead to minor improvements for Ag_2 and Au_2, although the excellent results presented in Sec. IV demonstrate that the single geminal approach is adequate for producing high-accuracy energies and spectroscopic properties.

IV. BENCHMARK CALCULATIONS

A. Atomic properties

The CCSD(T)-F12b results for atomic excitation energies, electron affinities, and ionization energies are shown in Table V and Tables S5–S8, respectively. Herein, the (aug-)cc-pV*n*Z-PP-F12 basis sets are abbreviated (a)V*n*Z-F12 and cc-pCV*n*Z-PP-F12 as CV*n*Z-F12. The matching auxiliary basis sets were used in all cases, along with a geminal exponent of 1.4 a_0^{-1}. The diffuse augmented basis sets developed in this work were used for the calculation of atomic properties as initial testing demonstrated a significant increase in accuracy, particularly at the DZ and TZ level. For all of the atomic and molecular benchmarks presented, the focus is on comparison with conventional results, rather than experiment, as this reflects the performance of explicitly correlated calculations and the newly developed basis sets. A meaningful comparison with experiment would also require consideration of additional factors, such as pseudopotential approximation errors and spin–orbit coupling, and these contributions to atomic and molecular properties have been considered elsewhere.[21]

The CCSD(T)-F12b $s^1d^{10} \rightarrow s^2d^9$ excitation energies for the coinage metals are shown in Table V, along with the CBS estimate from conventional CCSD(T) calculations taken from Ref. 21. There is a very rapid convergence toward the basis set limit for the valence-only energies, and a comparison with the data from Ref. 21, shown in the supplementary material, indicates that CCSD(T)-F12b/aVDZ-F12 produces results that are similar to or better than conventional 5Z. For Ag and Au, the aVQZ-F12 excitation energies are likely to be a more accurate reflection of the CBS limit than those estimated from conventional calculations, highlighting the slow basis set convergence in conventional calculations on these atoms. The convergence of the effect of correlating the $(m-1)$ sp electrons is even more rapid than the valence-only energies as the aCVDZ-F12 results are within 0.13 kcal mol^{-1} of aCVQZ-F12. Remarkably, these aCVDZ-F12 results are somewhere between conventional aCV5Z and CBS estimates. Similar trends in accuracy and convergence are observed for the electron affinities of the coinage metals and the ionization energies of group 11 and 12 atoms, with data presented in the supplementary material.

TABLE V. CCSD(T)-F12b excitation energies $s^1d^{10} \rightarrow s^2d^9$ for the group 11 atoms compared to conventional CBS estimates (kcal mol^{-1}) from Ref. 21.

	Valence only			$(m-1)$ sp correlation		
Basis set	Cu	Ag	Au	Cu	Ag	Au
a(C)VDZ-F12	33.10	95.65	44.54	+0.02	−6.51	−5.33
a(C)VTZ-F12	33.50	95.78	44.58	−0.01	−6.47	−5.24
a(C)VQZ-F12	33.66	95.95	44.69	+0.03	−6.45	− 5.20
Conventional CBS	33.71	95.82	44.54	+0.08	−6.33	−5.05

B. Molecular benchmark calculations

To demonstrate the effectiveness of the new basis sets in molecular calculations, CCSD(T)-F12b calculations were carried out on the coinage metal homonuclear diatomics and monofluorides to determine the spectroscopic constants (D_e, r_e, and ω_e) presented in Table VI. For the homonuclear dimers, the convergence rate of the spectroscopic constants was improved by using the fully diffuse augmented sets; hence, the aV*n*Z-F12 sets developed in this work were used for the valence-only calculations, while the aCV*n*Z-F12 sets were used in determining the effect of $(m-1)$ sp-electron correlation. The more strongly bound monofluorides did not require the additional high-angular momentum diffuse functions, so the (C)V*n*Z-F12 sets were used for the coinage metals. The cc-pV*n*Z-F12 basis sets of Peterson *et al.* were used for fluorine,[15] along with the matching MP2FIT and OptRI auxiliary sets.[45,52] The cc-pV*n*Z JKFIT sets of Weigend were also used for fluorine,[40] and the fluorine 1s electrons were treated with the frozen core approximation in all cases.

Focusing first on the diatomic molecules containing coinage metals results in Table VI, the convergence of the valence–only correlated spectroscopic constants is very fast, especially when compared to the slow convergence for the conventional method seen in previous benchmarks.[21] Results with the F12b ansatz and the new triple-zeta basis sets are very close to the CBS limits estimated from extrapolations based on the conventional quadruple- and quintuple-zeta sets [CBS(Q5)] taken from Ref. 21 and 22, while the QZ F12b results may represent more accurate CBS estimates than those from the conventional calculations. The DZ F12b results are also relatively accurate, with mean unsigned deviations from the CBS results of 0.69 kcal mol^{-1}, 0.0034 Å, and 2.1 cm^{-1} for D_e, r_e, and ω_e, respectively. The analogous deviations with conventional DZ are 3.74 kcal mol^{-1}, 0.0272 Å, and 12.0 cm^{-1}.

While it is clear that the basis sets developed in this work, in conjunction with explicitly correlated coupled cluster methods, have a significantly accelerated convergence toward the basis set limit compared to conventional analogs, it is also important to compare the performance of the basis sets when both are used in explicitly correlated methods. Figure 6 thus shows the convergence of both D_e and r_e for the diatomic molecules Cu_2, AgF, and AuF with both the new (aug-)cc-pV*n*Z-PP-F12 and existing

TABLE VI. Calculated CCSD(T)-F12b frozen-core (valence) and (*m* – 1) sp-electron correlation contributions [Δ(*m* – 1)sp] for spectroscopic constants of various ground state diatomic molecules containing coinage metals. CBS(Q5) results are conventional CCSD(T) results from Refs. 21 and 22 using correlation consistent basis sets.

		D_e (kcal mol^{-1})		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis	Valence	Δ(*m* – 1)sp	Valence	Δ(*m* – 1)sp	Valence	Δ(*m* – 1)sp
Cu_2	a(C)VDZ-F12	46.01	+0.05	2.2195	−0.0017	265.2	+1.4
	a(C)VTZ-F12	46.58	−0.02	2.2143	−0.0008	268.5	+1.2
	a(C)VQZ-F12	46.74	−0.02	2.2134	−0.0011	268.5	+1.3
	CBS(Q5)	46.62	−0.04	2.2146	−0.0007	268.6	+1.5
Ag_2	a(C)VDZ-F12	37.72	+1.16	2.5405	−0.0138	188.9	+5.3
	a(C)VTZ-F12	38.44	+1.02	2.5336	−0.0119	191.3	+4.7
	a(C)VQZ-F12	38.61	+1.02	2.5329	−0.0119	191.9	+4.8
	CBS(Q5)	38.45	+0.91	2.5339	−0.0108	191.5	+4.7
Au_2	a(C)VDZ-F12	50.01	+1.83	2.4945	−0.0126	184.9	+4.1
	a(C)VTZ-F12	50.94	+1.65	2.4897	−0.0115	186.2	+3.7
	a(C)VQZ-F12	51.24	+1.56	2.4887	−0.0108	186.7	+3.5
	CBS(Q5)	51.15	+1.45	2.4876	−0.0107	186.9	+3.5
CuF	(C)VDZ-F12	97.94	−1.03	1.7448	+0.0026	614.1	−3.8
	(C)VTZ-F12	99.00	−0.92	1.7427	+0.0030	618.9	−2.8
	(C)VQZ-F12	99.14	−0.88	1.7419	+0.0029	619.6	−2.3
	CBS(Q5)	99.02	⋯	1.7415	⋯	619.5	⋯
AgF	(C)VDZ-F12	81.39	−0.68	1.9864	−0.0079	510.6	+5.5
	(C)VTZ-F12	81.56	−0.59	1.9857	−0.0075	511.9	+5.3
	(C)VQZ-F12	81.59	−0.58	1.9857	−0.0076	511.6	+5.3
	CBS(Q5)	81.61	⋯	1.9861	⋯	510.5	⋯
AuF	(C)VDZ-F12	67.76	+0.09	1.9358	−0.0102	545.4	+9.1
	(C)VTZ-F12	68.35	+0.26	1.9351	−0.0093	547.7	+8.9
	(C)VQZ-F12	68.66	+0.29	1.9349	−0.0092	548.0	+9.1
	CBS(Q5)	68.80	⋯	1.9351	⋯	547.9	⋯

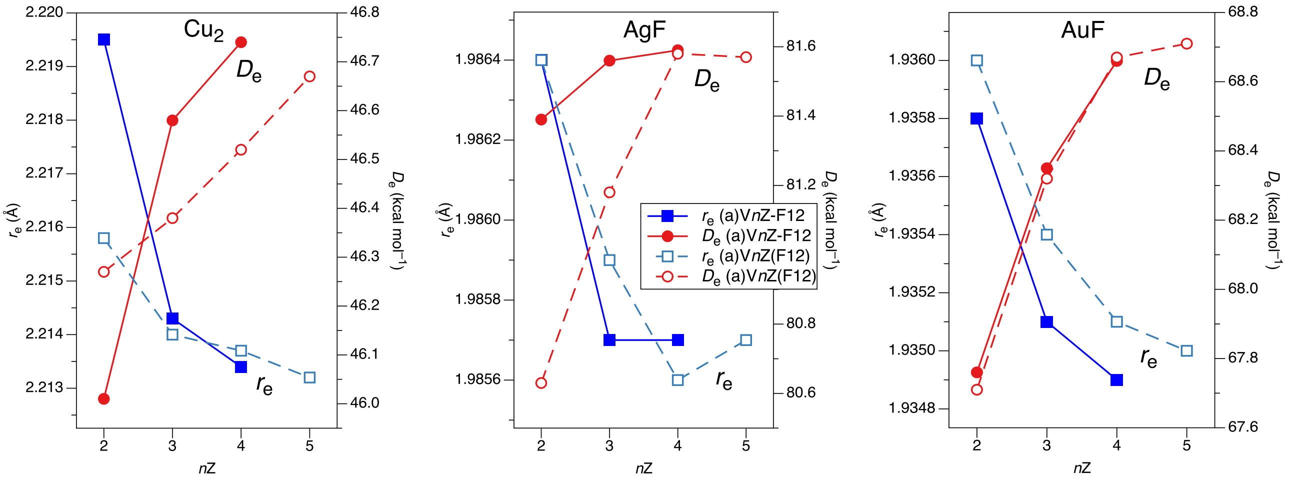

FIG. 6. Comparison of dissociation energy (D_e) and equilibrium bond length (r_e) of diatomic molecules calculated with basis sets developed in this work [(aug-)cc-pV*n*Z-PP-F12 abbreviated as (a)V*n*Z-F12, solid lines] and existing basis sets [(aug-)cc-pV*n*Z-PP abbreviated as (a)V*n*Z(F12), dashed lines]. In both cases, the data have been calculated at the CCSD(T)-F12b level of theory.

(aug-)cc-pV*n*Z-PP basis sets when both are used in CCSD(T)-F12b calculations. Focusing momentarily on Cu_2, it can be seen that while the conventional DZ basis outperforms that developed in this work in an absolute sense (i.e., closer to the data from the largest basis sets used), the convergence with respect to basis set size is greatly improved with those developed in this work. For example, the D_e with the existing basis sets follows an almost linear trend, suggesting no convergence, while that from the new sets resembles the typical monotonic pattern expected for correlation consistent basis sets. It is also noted that at the TZ and QZ level, the new basis sets produce results slightly better than those from $(n + 1)$Z existing sets. A similar improvement in the convergence pattern is also observed for the $Cu_2 r_e$.

The convergence with respect to basis sets plotted for AgF in Fig. 6 shows a somewhat similar trend to that for Cu_2; it is much improved when the basis sets developed in this work are used. In the case of the AgF D_e, the absolute values at the DZ and TZ level are also an improvement over using the conventional basis sets in explicitly correlated calculations. Unlike Cu_2 and AgF, the D_e and r_e values calculated for AuF displayed a smooth convergence when existing basis sets were used. A very similar convergence pattern is observed when using the basis sets of this work, and for D_e, the absolute values at any given zeta-level are also very similar. However, there is a noticeable improvement in r_e values with the new basis sets, particularly at the TZ and QZ level. Overall, it is clear that the basis sets developed in this work offer improved convergence over the conventional sets when both are used in F12 calculations, which will be important if extrapolation to the basis set limit is required. In a number of cases, there is also an improvement in the absolute values calculated using the new basis sets, which is often at the level of using an $(n + 1)$Z existing basis set, again in an F12 calculation. As the new, F12 specific basis sets are only 1s1p1d larger than those optimized for conventional calculations, the modest increase in computational cost is easily outweighed by ensuring smooth convergence with the basis set size.

Table VI also presents the effect of correlating the $(m - 1)$ sp-electrons on the spectroscopic constants of diatomic molecules containing coinage metals. As expected,[21] for Cu_2, these effects are almost zero and have very little basis set dependence. The effects are much larger for Ag_2 and Au_2 and are in good agreement with the conventional CCSD(T)/cc-pwCV*n*Z-PP results of Peterson and Puzzarini.[21] The convergence of the core–valence effect for both of these homonuclear diatomics is very rapid, suggesting that the effect can be successfully captured at the DZ level unless very high-accuracy is required. Similar levels of rapid convergence are also seen for the core–valence effect on the spectroscopic parameters of the coinage metal monofluorides.

Spectroscopic constants for the group 12 monofluorides have been computed using the basis sets developed in this work and are shown in Table VII. The convergence with respect to basis set is, again, very rapid, with DZ results within 1 kcal mol^{-1} of the CBS D_e estimated from conventional methods,[22] 0.0015 Å for r_e, and around 1 cm^{-1} for ω_e. The effect of correlating the $(m - 1)$ sp-electrons also converges very quickly, in a similar manner as observed for the coinage metal analogs.

Calculating accurate spectroscopic constants of the group 12 homonuclear diatomics is challenging as they are very weakly bound van der Waals dimers and a strong dependence on basis set has been observed. A study using conventional CCSD(T) demonstrated that doubly augmented d-aug-cc-pV*n*Z-PP basis sets were required to avoid incredibly slow convergence to the basis set limit.[21] This makes these van der Waals dimers an interesting test case for explicitly correlated methods and the basis sets developed in this work; is it possible to avoid the need for the very diffuse basis functions found in d-aug-cc-pV*n*Z-PP sets while still achieving a rapid convergence toward the CBS limit? The CCSD(T)-F12b/aug-cc-pV*n*Z-PP-F12 results are shown in Table VIII, where they are also compared to the conventional CCSD(T)/d-aug-cc-pV*n*Z-PP values of Peterson and Puzzarini.[21] Counterpoise corrections were used throughout, and it was observed that the use of an F12 method significantly

TABLE VII. Calculated CCSD(T)-F12b frozen-core (valence) and $(m - 1)$ sp-electron correlation contributions [$\Delta(m - 1)$sp] for spectroscopic constants of the $X^1\Sigma^+$ states of ZnF, CdF, and HgF. CBS(Q5) results are conventional CCSD(T) results from Ref. 22 using correlation consistent basis sets.

		D_e (kcal mol^{-1})		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis	Valence	$\Delta(m - 1)$sp	Valence	$\Delta(m - 1)$sp	Valence	$\Delta(m - 1)$sp
ZnF	(C)VDZ-F12	69.77	−0.75	1.7625	+0.0018	634.8	−0.8
	(C)VTZ-F12	70.30	−0.70	1.7629	+0.0018	634.0	−0.8
	(C)VQZ-F12	70.44	−0.70	1.7633	+0.0018	633.4	−1.2
	CBS(Q5)	70.43	⋯	1.7637	⋯	633.9	⋯
CdF	(C)VDZ-F12	59.37	−1.16	1.9766	−0.0026	538.2	+1.3
	(C)VTZ-F12	59.45	−1.07	1.9774	−0.0024	537.8	+1.1
	(C)VQZ-F12	59.56	−1.08	1.9780	−0.0025	536.9	+1.5
	CBS(Q5)	59.64	⋯	1.9785	⋯	535.4	⋯
HgF	(C)VDZ-F12	31.08	−0.98	2.0253	−0.0050	484.6	+2.2
	(C)VTZ-F12	31.42	−0.80	2.0253	−0.0044	485.1	+1.8
	(C)VQZ-F12	31.74	−0.77	2.0251	−0.0045	485.4	+1.9
	CBS(Q5)	31.86	⋯	2.0253	⋯	485.2	⋯

TABLE VIII. Calculated counterpoise corrected CCSD(T)-F12b frozen-core spectroscopic constants of the $X^1\Sigma_g^+$ states of the group 12 homonuclear van der Waals dimers. Conventional CCSD(T) results from Ref. 21 with the doubly augmented correlation consistent basis sets (d-aV*n*Z).

Molecule	Method	Basis	D_e (cm^{-1})	r_e (Å)	ω_e (cm^{-1})
Zn_2	CCSD(T)	d-aVDZ	135.4	4.2048	17.6
		d-aVTZ	183.7	3.9538	21.1
		d-aVQZ	205.8	3.8910	22.0
		d-aV5Z	218.1	3.8619	23.1
	CCSD(T)-F12b	aVDZ-F12	185.8	3.9221	21.2
		aVTZ-F12	210.2	3.8568	22.8
		aVQZ-F12	222.7	3.8466	23.3
Cd_2	CCSD(T)	d-aVDZ	219.6	4.1794	16.8
		d-aVTZ	282.5	3.9864	19.3
		d-aVQZ	307.6	3.9318	20.5
		d-aV5Z	315.1	3.9256	20.2
	CCSD(T)-F12b	aVDZ-F12	260.3	4.0016	18.8
		aVTZ-F12	309.1	3.9178	20.6
		aVQZ-F12	324.1	3.8974	20.9
Hg_2	CCSD(T)	d-aVDZ	228.9	4.0623	14.8
		d-aVTZ	317.4	3.8368	17.5
		d-aVQZ	350.1	3.7858	18.4
		d-aV5Z	361.5	3.7530	18.5
	CCSD(T)-F12b	aVDZ-F12	277.4	3.8984	16.1
		aVTZ-F12	345.6	3.7837	18.5
		aVQZ-F12	363.3	3.7525	18.7

reduced the basis set superposition error; the effect of the counterpoise correction on spectroscopic constants at the DZ level with the F12 method was approximately the same as that at the QZ level and conventional method. This follows the general trend observed for lighter elements.[57,58]

Figure S6 in the supplementary material plots D_e and r_e, where it can be seen that F12 using the new basis sets produces results that are of similar quality to the conventional method with the d-aug-cc-pV($n + 1$)Z-PP basis, without requiring the additional very diffuse functions that can cause numerical problems in some cases. The convergence in D_e is rapid, with the DZ-F12 result only a maximum of 86 cm^{-1} (~0.25 kcal mol^{-1}) from the QZ-F12 value. However, convergence in r_e is perhaps a little slower than desired, despite being improved over the conventional method and basis. A possible route to improving this in the future may be through the use of midbond functions designed for use in explicitly correlated calculations.[59,60]

V. CONCLUSIONS

Correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements have been developed for use in explicitly correlated F12 calculations based on the small-core relativistic PPs of Figgen *et al.*[20] Orbital basis sets for valence only correlation (cc-pV*n*Z-PP-F12, n = D, T, Q) have been reported, along with those for outer-core correlation (cc-pCV*n*Z-PP-F12) and both these basis sets extended with additional high angular momentum diffuse functions. The auxiliary basis sets required to use the above in F12 calculations have also been developed, including those for density fitting of the Fock and exchange matrices (JKFIT) and density fitting of the remaining two-electron integrals (MP2FIT) and for use in the CABS procedure for the evaluation of the many-electron integrals arising in F12 theory (OptRI). Atomic and molecular benchmark calculations were run at the CCSD(T)-F12b level with the new basis sets for both valence-only and core–valence electron correlation and then compared to previously published conventional CCSD(T) results. Using the new basis sets with the F12 method leads to very rapid convergence of atomic excitation energies, electron affinities, and ionization energies, with double-zeta basis sets producing F12 results that are roughly equivalent to those from conventional five-zeta calculations.

Benchmarking of the new basis sets on diatomic molecules produces a similar picture, and the convergence toward the CBS limit is rapid, even for the challenging group 12 van der Waals dimers. The convergence of the core–valence effect on spectroscopic properties of diatomic molecules is perhaps even quicker than the valence-only convergence, with only a small variation between double-zeta and quadruple-zeta. The dissociation energy and equilibrium bond length calculated in this work were compared to previously published values for conventional basis sets used in F12 calculations. An improvement in the performance with respect to basis set was observed for the basis sets presented here, particularly for the convergence toward the basis set limit, which will be important for basis set extrapolation of F12 results. Overall, the rapid and smooth convergence observed with the new basis sets paves the way for explicitly correlated calculations on large molecules containing group 11 or 12 elements.

All of the orbital and auxiliary basis sets developed in this work are provided in the supplementary material and will also be made available for download from the correlation consistent basis set repository.[61]

SUPPLEMENTARY MATERIAL

See the supplementary material for the basis sets developed in this work in a machine readable format, geometries of molecules in the test set, comparisons of basis sets sizes and compositions, scans of the geminal Slater exponent, and further benchmarking data.

ACKNOWLEDGMENTS

The authors thank the UK Engineering and Physical Sciences Research Council (EPSRC) for support through Grant No. EP/T027134/1.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

[1] D. Feller, K. A. Peterson, and J. G. Hill, J. Chem. Phys. **135**, 044102 (2011).
[2] V. Vasilyev, Comput. Theor. Chem. **1115**, 1 (2017).
[3] A. J. C. Varandas, Annu. Rev. Phys. Chem. **69**, 177 (2018).
[4] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chem. Rev. **112**, 4 (2012).
[5] L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112**, 75 (2012).
[6] T. Shiozaki and H.-J. Werner, Mol. Phys. **111**, 607 (2013).
[7] A. Grüneis, S. Hirata, Y. Ohnishi, and S. Ten-no, J. Chem. Phys. **146**, 080901 (2017).
[8] H.-J. Werner, T. B. Adler, and F. R. Manby, J. Chem. Phys. **126**, 164102 (2007).
[9] H. Fliegl, W. Klopper, and C. Hättig, J. Chem. Phys. **122**, 084107 (2005).
[10] D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, Phys. Chem. Chem. Phys. **9**, 1921 (2007).
[11] T. B. Adler, G. Knizia, and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[12] G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130**, 054104 (2009).
[13] T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011).
[14] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[15] K. A. Peterson, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **128**, 084102 (2008).
[16] J. G. Hill and K. A. Peterson, Phys. Chem. Chem. Phys. **12**, 10460 (2010).
[17] K. A. Peterson, M. K. Kesharwani, and J. M. L. Martin, Mol. Phys. **113**, 1551 (2014).
[18] J. G. Hill and K. A. Peterson, J. Chem. Phys. **141**, 094106 (2014).
[19] J. G. Hill, S. Mazumder, and K. A. Peterson, J. Chem. Phys. **132**, 054108 (2010).
[20] D. Figgen, G. Rauhut, M. Dolg, and H. Stoll, Chem. Phys. **311**, 227 (2005).
[21] K. A. Peterson and C. Puzzarini, Theor. Chem. Acc. **114**, 283 (2005).
[22] J. G. Hill and K. A. Peterson, J. Chem. Theory Comput. **8**, 518 (2012).
[23] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. Miller III, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, T. Petrenko, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and M. Welborn, MOLPRO, version 2020.1, a package of *ab initio* programs, 2020, see http://www.molpro.net.
[24] H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Hesselmann, D. Kats, A. Köhn, T. Korona, D. A. Kreplin, Q. Ma, T. F. Miller III, A. Mitrushchenkov, K. A. Peterson, I. Polyak, G. Rauhut, and M. Sibaev, J. Chem. Phys. **152**, 144107 (2020).
[25] S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński, and J. M. Yu, J. Chem. Phys. **152**, 184107 (2020).
[26] TURBOMOLE V7.4.1 2019, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[27] J. L. Dunham, Phys. Rev. **41**, 721 (1932).
[28] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
[29] F. Weigend, J. Comput. Chem. **29**, 167 (2008).
[30] E. F. Valeev, Chem. Phys. Lett. **395**, 190 (2004).
[31] T. Shiozaki and H.-J. Werner, J. Chem. Phys. **134**, 184104 (2011).
[32] N. B. Balabanov and K. A. Peterson, J. Chem. Phys. **123**, 064107 (2005).
[33] J.-P. Blaudeau, S. R. Brozell, S. Matsika, Z. Zhang, and R. M. Pitzer, Int. J. Quantum Chem. **77**, 516 (2000).
[34] P. A. Christiansen, J. Chem. Phys. **112**, 10070 (2000).
[35] D. Manna, M. K. Kesharwani, N. Sylvetsky, and J. M. L. Martin, J. Chem. Theory Comput. **13**, 3136 (2017).
[36] N. Sylvetsky, M. K. Kesharwani, and J. M. L. Martin, J. Chem. Phys. **147**, 134106 (2017).
[37] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).
[38] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).
[39] K. A. Peterson, D. Figgen, M. Dolg, and H. Stoll, J. Chem. Phys. **126**, 124101 (2007).
[40] F. Weigend, Phys. Chem. Chem. Phys. **4**, 4285 (2002).
[41] F. Weigend, Phys. Chem. Chem. Phys. **8**, 1057 (2006).
[42] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[43] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[44] A. Schaefer, H. Horn, and R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992).
[45] S. Kritikou and J. G. Hill, J. Chem. Theory Comput. **11**, 5269 (2015).
[46] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).
[47] C. Hättig, Phys. Chem. Chem. Phys. **7**, 59 (2005).
[48] C. Hättig and F. Weigend, J. Chem. Phys. **113**, 5154 (2000).
[49] C. Hättig, J. Chem. Phys. **118**, 7751 (2003).
[50] D. W. Schwenke, J. Chem. Phys. **122**, 014107 (2005).
[51] J. G. Hill, K. A. Peterson, G. Knizia, and H.-J. Werner, J. Chem. Phys. **131**, 194105 (2009).
[52] K. E. Yousaf and K. A. Peterson, J. Chem. Phys. **129**, 184108 (2008).
[53] R. A. Shaw and J. G. Hill, J. Chem. Theory Comput. **13**, 1691 (2017).
[54] S. Höfener, D. P. Tew, W. Klopper, and T. Helgaker, Chem. Phys. **356**, 25 (2009).
[55] H.-J. Werner, G. Knizia, and F. R. Manby, Mol. Phys. **109**, 407 (2011).
[56] K. A. Peterson, C. Krause, H. Stoll, J. G. Hill, and H.-J. Werner, Mol. Phys. **109**, 2607 (2011).

[57] B. Brauer, M. K. Kesharwani, and J. M. L. Martin, J. Chem. Theory Comput. **10**, 3791 (2014).
[58] N. Sylvetsky, K. A. Peterson, A. Karton, and J. M. L. Martin, J. Chem. Phys. **144**, 214101 (2016).
[59] F. M. Tao and Y. K. Pan, J. Chem. Phys. **97**, 4989 (1992).
[60] R. A. Shaw and J. G. Hill, Mol. Phys. **116**, 1460 (2018).
[61] Correlation consistent basis set repository, http://bit.ly/ccBasis; accessed October 13, 2021.