The Journal of Chemical Physics

RESEARCH ARTICLE | MARCH 15 2024

Diffuse basis functions for explicitly correlated calculations on the heavy p-block: aug-cc-pV*n*Z-PP-F12 sets for Ga–Kr, In–Xe, and Tl–Rn

J. Grant Hill

J. Chem. Phys. 160, 114102 (2024)
https://doi.org/10.1063/5.0197210

AIP Publishing

The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

Diffuse basis functions for explicitly correlated calculations on the heavy p-block: aug-cc-pV*n*Z-PP-F12 sets for Ga–Kr, In–Xe, and Tl–Rn

Cite as: J. Chem. Phys. 160, 114102 (2024); doi: 10.1063/5.0197210
Submitted: 12 January 2024 • Accepted: 28 February 2024 •
Published Online: 15 March 2024

J. Grant Hill[a)]

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 aug-cc-pV*n*Z-PP-F12 basis sets (n = D, T, Q) for the heavy p-block elements, Ga–Kr, In–Xe, and Tl–Rn, have been developed by augmenting the cc-pV*n*Z-PP-F12 sets with additional higher angular momentum diffuse functions. These basis sets have been optimized for use in explicitly correlated F12 calculations, and matching auxiliary basis sets for density fitting of conventional and F12 integrals have also been developed. The new sets have been validated with benchmark CCSD(T)-F12b calculations of electron affinities, where an accelerated convergence to the complete basis set limit is evident. The effect of the additional diffuse functions on electron affinities is shown to be comparable to the effect of correlating the outer-core d electrons.

I. INTRODUCTION

In the domain of high-accuracy molecular electronic structure calculations, the move to explicitly correlated methods has sparked a dramatic improvement in the convergence of correlation energy and other properties with respect to basis set size.[1–3] Previously, methods such as the coupled cluster (CC)[4] approximation were limited by a requirement for large basis sets to reach convergence and simultaneous steep scaling of the necessary computational resources. One solution to this problem has been to use basis sets that systematically approach the complete basis set (CBS) limit, such as the correlation consistent family,[5] and then estimate the CBS limit using extrapolation formulae; with correlation consistent polarized valence n-zeta (cc-pV*n*Z) basis sets, one can take energies computed with two or more different basis set cardinal numbers, n, and after selecting a suitable extrapolation formula (see, for example, Refs. 6–8 for more information on such extrapolations), easily produce a CBS estimate. The explicitly correlated (F12) methods offer a different approach; the inclusion of geminal terms that depend on the interelectronic distance greatly accelerates convergence toward the CBS limit.

The development and technical details of F12 methods have been the subject of several reviews[1–3,9] and will not be introduced in detail here. From the perspective of modern electronic structure package users, carrying out an F12 calculation has become somewhat routine, and requesting an explicitly correlated coupled-cluster calculation is generally no more difficult than the equivalent conventional coupled-cluster method. Selecting some examples from the literature, by using F12 methods, it is possible to obtain "quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets,"[10] and basis set extrapolations of conventional correlation energies with quadruple-zeta (QZ) and 5Z basis sets have been found to produce results somewhere between explicitly correlated TZ and QZ (without extrapolation).[11] While this level of performance may not be achieved in every application, in general, F12 methods do resolve some of the basis set convergence problems typical of high-accuracy *ab initio* methods. There are also basis set extrapolation formulae that take into account the faster convergence of F12 methods.[12–14]

The ease of use of F12 methods has been enabled by benchmarking studies and basis set development that has produced sensible default settings to be adopted for general usage,

such as the selection of auxiliary basis sets and the exponent of the Slater-type geminal. Of course, these defaults may differ between electronic structure codes, and potentially between different releases/versions of a given code. Both density fitting (DF) and resolution of the identity (RI) techniques are used for the robust approximation of electronic integrals in the majority of implementations of F12 theory. The DF and RI names are sometimes used interchangeably by some authors, but herein, DF is used to signify the approximation of integrals used in the DF-HF and DF-MP2 methods,[15–17] and RI is reserved for the evaluation of F12-specific integrals.[18] This leads to F12 methods requiring three separate auxiliary basis sets (ABSs), in addition to the orbital basis set (OBS). Using the naming convention from the Molpro system of *ab initio* programs,[19,20] these ABSs are the JKFit basis used in the evaluation of the Coulomb and exchange matrices, the MP2Fit basis used in density fitting of conventional two-electron repulsion integrals (i.e., those from the DF-MP2 method), and an RI or complementary auxiliary basis set (CABS) for the F12-specific integrals.

The nonlinear correlation factors included in F12 wavefunctions are of the form $\exp(-\gamma r_{12})$, where γ is the geminal Slater exponent (see Ref. 21 and references therein). The optimal value of γ depends on the chemical system, the orbital basis set, and the electrons being correlated. For example, a γ value of 1.4 a_0^{-1} has been found to work well for the core electron correlation effects on lighter p-block elements,[22] but values closer to 1.0 a_0^{-1} produce energetically favorable results for valence-only correlation.[12] For some elements, particularly those further down the Periodic Table, appropriate basis sets (orbital and/or auxiliary) and γ values for the calculation of energies and/or properties with F12 methods have not yet been established.

Orbital basis sets specifically optimized for use in F12 calculations display a smoother convergence toward the CBS limit (when used in F12 calculations) than conventionally optimized basis sets.[23,24] For full details of the development of correlation consistent basis sets for use in F12 calculations,[22–27] which are often abbreviated to V*n*Z-F12, the interested reader is referred to Ref. 23, but as a high-level outline, they are typically optimized at the MP2-F12 level of theory and aim to balance the basis set incompleteness errors in both the Hartree–Fock and correlated components of the total energy. To address the latter point, a given V*n*Z-F12 orbital basis includes, for elements from the second and third periods, the (HF-like) s and p functions from the aug-cc-pV(n + 1)Z basis.[28] The exponents of the optimized correlating functions with the orbital basis are also usually more diffuse than those from an equivalent correlation consistent basis for use in conventional correlated calculations. Of particular relevance to the present work are the cc-pV*n*Z-PP-F12 basis sets for the heavy p-block elements Ga–Kr, In–Xe, and Tl–Rn.[26] These basis sets are constructed for use with the Stuttgart–Cologne small-core relativistic pseudopotentials (PPs),[29–32] and although PPs are used for all of the heavy p-block elements, the simple abbreviation V*n*Z-F12 is used to refer to these sets herein.

Although the V*n*Z-F12 orbital sets do contain some diffuse functions for the lower angular momentum symmetries, it has been demonstrated that the accurate calculation of electron affinities (EAs) and non-covalent interactions requires additional augmentation of the basis sets with higher angular momentum diffuse functions.[33] Such basis sets have been developed for the elements H, B–Ne, and Al–Ar and are denoted aug-cc-pV*n*Z-F12 (or aV*n*Z-F12 for short). The exponents for these additional diffuse functions were optimized for the atomic anions at the MP2-F12 level of theory, with exponents for N, Ne, and Ar determined by cubic interpolation.

The primary aim of this work is thus to augment the existing cc-pV*n*Z-PP-F12 basis sets for the heavy p-block elements (Ga–Kr, In–Xe, and Tl–Rn) with additional higher-angular momentum diffuse functions to improve their performance in calculations on anions. Section II describes the basis set development and optimization process, including that for the required ABSs. Sections III and IV then describe the computational methods used and the results of the in-depth benchmarking of the new basis sets for calculating electron affinities.

II. BASIS SET DEVELOPMENT

A. Orbital basis sets

The new aug-cc-pV*n*Z-PP-F12 (n = D, T, Q) orbital basis sets have been produced by augmenting the existing cc-pV*n*Z-PP-F12 sets with additional diffuse functions, keeping all other exponents in the basis fixed. As the parent cc-pV*n*Z-PP-F12 sets already contain diffuse s- and p-type functions from the aug-cc-pV(n + 1)Z-PP sets, augmenting functions were only added for higher angular momentum shells already occupied in the cc-pV*n*Z-PP-F12 parent. It should be noted that the cc-pVDZ-PP-F12 basis contains f-type functions, but the purpose of these functions is for (optional) correlation of the outer-core d electrons; hence, the decision was taken to only add diffuse d functions in the DZ case. As a single additional exponent is added for each angular momentum symmetry concerned, at the DZ level, the parent basis is augmented by 1d exponent, 1d1f at the TZ level, and 1d1f1g at the QZ level. This process is analogous to the diffuse augmentation of the cc-pV*n*Z-F12 sets undertaken by Sylvertsky *et al.*[33] The basis set compositions for the new aug-cc-pV*n*Z-PP-F12 sets are summarized in Table I, where they are also compared to the respective cc-pV*n*Z-PP-F12 composition.

The exponents of the augmenting diffuse functions were determined by optimizing the MP2-F12 energy for the lowest electronic state of the atomic anions, using the Nelder–Mead simplex algorithm in Molpro's general purpose optimizer.[19,20,34] In terms of ABSs, these optimizations used the large even-tempered (18s17p15d12f10g8h7i) "reference" sets described in Ref. 26 as

TABLE I. Composition of the diffuse augmented orbital basis sets of this work (aug-cc-pV*n*Z-PP-F12) compared to the parent cc-pV*n*Z-PP-F12 of Ref. 26.

Element	Zeta-level	aug-cc-pV*n*Z-PP-F12	cc-pV*n*Z-PP-F12
4p	DZ	[6s5p5d1f]	[6s5p4d1f]
	TZ	[7s6p6d4f]	[7s6p5d3f]
	QZ	[8s7p7d5f3g]	[8s7p6d4f2g]
5p and 6p	DZ	[6s5p5d1f]	[6s5p4d1f]
	TZ	[7s7p6d4f]	[7s7p5d3f]
	QZ	[8s8p7d5f3g]	[8s8p6d4f2g]

both MP2Fit and RI bases. All of the F12 calculations using diffuse augmented orbital basis sets use a modified version of the def2-QZVPP-JKFit ABS of Weigend in the density fitting of the exchange and Coulomb integrals.[35] The modification takes the form of a single additional diffuse exponent added to each angular symmetry in an even-tempered fashion. The resulting ABS is known as def2-AQZVPP-JKFit in the Molpro basis set library. A geminal Slater exponent of 1.4 a_0^{-1} was used, along with the 3C ansatz,[36] consistent with the development of the cc-pVnZ-PP-F12 parent sets.

For the group 18 elements Kr, Xe, and Rn, where the atomic anion is unbound, the exponent of the additional diffuse functions was determined by extrapolation of the optimized exponents for elements in the same row (restricted to the p-block). For example, the DZ diffuse d exponent for Kr was determined based upon the DZ diffuse d exponents for Ga–Br. Visual inspection and curve fitting of the exponents across the relevant part of the p-block of the Periodic Table was used to determine if a linear, second-order polynomial, or exponential function was the most appropriate to use in determining the new exponent. The functional form used for each combination of group 18 element and basis set is detailed in the supplementary material, along with the freely optimized exponents/basis sets for the other heavy p-block elements.

B. MP2Fit auxiliary basis sets

When considering orbital basis sets augmented with extra diffuse functions, the usual approach to constructing matching MP2Fit ABSs is to take the existing ABS and optimize one additional diffuse primitive for each angular symmetry in that ABS.[37] For example, the cc-pVTZ-MP2Fit basis for Ge contains functions with s–h angular momentum; hence, aug-cc-pVTZ-MP2Fit adds one additional primitive for each of s–h.[38] The exponents of these additional primitives are optimized for the ground state of the anions of the atom by minimizing the following objective function:

$$\delta_{\mathrm{DF}} = -\frac{1}{4}\sum_{aibj}\frac{\left(\langle ab\|ij\rangle_{\mathrm{DF}} - \langle ab\|ij\rangle\right)^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j},$$

where $\langle ab\|ij\rangle$ denotes two-electron repulsion integrals, ϵ_x are orbital energies, i and j are occupied orbitals, and a and b are virtual orbitals.[39] The error in the MP2 correlation energy due to density fitting (ΔDF) is also an important metric when analyzing the performance of ABSs, where $\Delta\mathrm{DF} = E^{\mathrm{corr}}_{\mathrm{DF-MP2}} - E^{\mathrm{corr}}_{\mathrm{MP2}}$.

In the present case, adding an additional diffuse function for every angular symmetry occupied in the cc-pVnZ-PP-F12-MP2Fit ABS would not produce an efficient auxiliary basis as too many functions would be added. The aug-cc-pVnZ-PP-F12 orbital basis sets only add diffuse functions of higher angular symmetry, and the cc-pVnZ-PP-F12-MP2Fit ABSs of Ref. 26 are specifically matched to orbital sets that contain diffuse s and p functions. To determine how many functions of each angular symmetry to add, we first calculate δ_{DF} and ΔDF using the cc-pVnZ-PP-F12 OBS and MP2Fit combination for the anion of the atoms Se, Te, and Po. These calculations are carried out using the RICC2 module of the TURBOMOLE program,[40–43] which features analytical gradients for the optimization of MP2Fit ABSs.[44] The goal then becomes to achieve similar values of δ_{DF} and ΔDF when the aug-cc-pVnZ-PP-F12 orbital basis is used. This is explored by first using the cc-pVnZ-PP-F12-MP2Fit ABSs and then augmenting with additional functions whose exponents are optimized to minimize δ_{DF}. The results of this exploration exercise for the Te anion with TZ quality sets are shown in Table II, where the $(m-1)$d electrons are treated with the frozen-core approximation.

TABLE II. Density fitting errors in the two-electron repulsion integrals (δ_{DF}) and MP2 correlation energy (ΔDF) for the anion of the Te atom. The VTZ-F12-MP2Fit ABS is augmented with a series of additional diffuse functions. In the case of even1f1g, the exponents of the additional functions are determined by even-tempered extension, rather than free optimization.

OBS	MP2Fit ABS	δ_{DF} (ppm)	ΔDF (μE_{h})
VTZ-F12	VTZ-F12	5.25×10^{-2}	−0.73
aVTZ-F12	VTZ-F12	5.66×10^{1}	−16.42
	VTZ-F12 + 1d	5.70×10^{1}	−16.39
	VTZ-F12 + 1f	5.41×10^{1}	−15.36
	VTZ-F12 + 1g	2.63×10^{0}	−1.20
	VTZ-F12 + 1f1g	4.62×10^{-2}	−0.14
	VTZ-F12 + even1f1g	4.65×10^{-2}	−0.10

From Table II, it can be seen that adding an additional set of g functions to the ABS (denoted "VTZ-F12 + 1g") produces a significant reduction in the density fitting error metrics, including greater than an order of magnitude improvement in the accuracy of the DF-MP2 correlation energy. Perhaps more significantly, adding a combination of both f and g functions results in density fitting errors that are roughly on a par with the baseline results observed for the VTZ-F12 OBS paired with the matching MP2Fit ABS. An alternative to freely optimizing the exponents of these f and g exponents is also explored, namely an even-tempered extension of the existing exponents. In this extension, the two most diffuse functions in a specific angular shell, ζ_1^l and ζ_2^l, are used to define the new diffuse exponent as $\zeta^l_{\mathrm{diffuse}} = \zeta_1^l/(\zeta_2^l/\zeta_1^l)$. Table II shows that this even-tempered extension ("even1f1g") produces density fitting errors that are approximately the same as those from freely optimized exponents. Similar explorations at the DZ and QZ level (see the supplementary material) show that even-tempered extensions also produce satisfactory results, with DZ requiring one additional f exponent and QZ requiring 1f1g1h. The supplementary material also shows that augmenting the ABSs with the same patterns of even-tempered extensions produces negligible density fitting errors for Se and Po.

Based on the above analysis, aVnZ-F12-MP2Fit ABSs were then generated for all of the heavy p-block elements by even-tempered extension of the VnZ-F12 auxiliary sets. At the DZ level, this extension was 1f exponent; at TZ, this extension was 1f1g; and at QZ, this extension was 1f1g1h. The resulting auxiliary basis sets are presented in the supplementary material.

C. Complementary auxiliary basis set for use in F12 methods

As mentioned in the Introduction, F12 calculations require an RI auxiliary basis set for the evaluation of the additional multielectron integrals, which is typically implemented using the

complementary auxiliary basis set (CABS+) approach.[45] RI auxiliary sets have been developed to specifically match the cc-pVnZ-F12 family of orbital basis sets and are commonly known as OptRI sets.[46] They are designed to be compact and lead to a linearly independent CABS basis. That is, when a union of the OptRI and orbital basis is formed, no functions will be deleted in the CABS procedure. The exponents of the OptRI sets are optimized to minimize the value of $\sqrt{\delta_{\mathrm{RI}}}$ for the ground state of neutral atoms, where

$$\delta_{\mathrm{RI}} = \sum_{ij} \frac{\left(V_{ij,ij} - V^{\mathrm{ref}}_{ij,ij}\right)^2}{|V^{\mathrm{ref}}_{ij,ij}|} + \frac{\left(B_{ij,ij} - B^{\mathrm{ref}}_{ij,ij}\right)^2}{|B^{\mathrm{ref}}_{ij,ij}|}. \quad (1)$$

The **V** and **B** matrices used in the evaluation of δ_{RI} are obtained from MP2-F12 calculations, and the interested reader is referred to Ref. 36 for further details of their definition. In essence, δ_{RI} is concerned with the difference in the **V** and **B** matrices using two different auxiliary sets: the candidate set being optimized and a reference set [denoted by a ref superscript in Eq. (1)], which is typically taken to be large and near-complete. Thus, minimizing the value of $\sqrt{\delta_{\mathrm{RI}}}$ for an appropriate number and composition of functions should produce an RI basis that introduces negligible errors in the approximated integrals. The difference in MP2-F12 correlation energy between a candidate RI basis and the reference basis is also of interest and is denoted ΔRI.

OptRI sets matched to the cc-pVnZ-PP-F12 orbital sets for the heavy p-block elements are available,[26] and the present aim is to adapt these auxiliary sets for the aug-cc-pVnZ-PP-F12 orbital sets also developed in this work. Matching previous development of OptRI sets, the 3C ansatz was used along with a geminal Slater exponent of 1.4 a_0^{-1}. The $(m-1)$d electrons were included in the frozen-core approximation, and a steep penalty function was applied such that the ratio between any new exponent and an existing exponent, in either the orbital or auxiliary basis, is greater than or equal to 1.3. All calculations involving δ_{RI} were carried out in a locally modified version of the Molpro package, with optimizations using the Nelder–Mead simplex algorithm. The reference ABS used was the large, even-tempered set used in the orbital basis set development.

To establish a set of baseline values, δ_{RI} and ΔRI were calculated for the neutral atoms using the cc-pVnZ-PP-F12 OBS and matching OptRI ABS. Analogous values were then also computed for the anion of the atoms using the newly developed aug-cc-pVnZ-PP-F12 OBS and the cc-pVnZ-PP-F12-OptRI ABS, with the difference between the two sets of values highlighting any deficiencies in the latter combination. Data for Te are presented in Table III as an example, where, perhaps unsurprisingly, it can be seen that for all zeta levels, both the metric for the error in integrals and the error in the MP2-F12 correlation energy increase for the anion. The goal in developing an aug-cc-pVnZ-PP-F12-OptRI set then becomes for the anion error metrics to be equivalent to (or better than) those for the neutral atom.

To achieve the above goal, an additional (optimized for the atomic anion) diffuse function was incrementally added to each angular symmetry in the cc-pVnZ-PP-F12-OptRI ABS and then discarded if the resulting change in the error metrics was negligible. The number of functions retained depended on both the zeta level of the orbital basis and which row of the Periodic Table the element belonged to. The latter could perhaps have been anticipated as the composition of the parent cc-pVnZ-PP-F12-OptRI sets also varies with row. Final compositions of the resulting aug-cc-pVnZ-PP-F12-OptRI sets are presented in the supplementary material, along with the optimized exponents. For the 4p elements, DZ was augmented with 1g function and TZ with 1i. 5p required 1f at DZ level and 1f1g1h1i at TZ, while 6p needed 1h at DZ and 1i at TZ. For all three rows, the QZ parent set was augmented with 1h1i functions. The exponents for the group 18 elements were determined by extrapolation of the optimized exponents for other elements in the same row, in a similar fashion as for the orbital basis sets. The functional form used for this extrapolation is given in the supplementary material.

TABLE III. RI errors (relative to the reference ABS) when using the cc-pVnZ-PP-F12-OptRI ABS for the neutral and anion Te atom. Calculations on the neutral atom use the cc-pVnZ-PP-F12 orbital basis, while aug-cc-pVnZ-PP-F12 is used for the anion. The values of the integral error metric, δ_{RI}, are expressed as parts per billion (ppb) due to their small size.

Zeta level	Charge	δ_{RI} (ppb)	ΔRI (μE_{h})
DZ	Neutral	3.63	−3.45
	Anion	5.38	−14.43
TZ	Neutral	18.48	−3.25
	Anion	22.08	6.48
QZ	Neutral	28.76	3.96
	Anion	31.34	7.63

The distributions of both δ_{RI} and ΔRI for the DZ quality basis sets are shown in Fig. 1 as violin plots. It can be seen that both error metrics change significantly when the cc-pVDZ-PP-F12-OptRI basis is used for the anion of the atom (middle distribution in each panel), but the error distributions resulting from the new aug-cc-pVDZ-PP-F12-OptRI set for the anion (rightmost distribution) closely resemble those when cc-pVDZ-PP-F12-OptRI is used for the neutral atom (leftmost), which meets the qualitative aim outlined above and hence indicates a similar quality of RI approximation for the anion as for the neutral atom. Violin plots of the RI errors at the TZ and QZ levels are presented in the supplementary material, where similar trends can be seen.

For the first and second row elements, adding tight s and p functions to the OptRI basis produced a significant increase in the CABS singles correction to the Hartree–Fock energy, resulting in the OptRI + auxiliary sets.[47] As part of the development of the present RI sets, the effect of adding tight s, p, and d functions in the CABS singles correction was also examined, but it was found to be negligible.

III. COMPUTATIONAL METHODOLOGY

The atomic electron affinities (EAs) are calculated as

$$\mathrm{EA} = E(\mathrm{neutral}) - E(\mathrm{anion})$$

at the CCSD(T)-F12b level of theory using the Molpro package.[48–50] The Molpro default ansatz of 3C(FIX) was used,[51] along with a

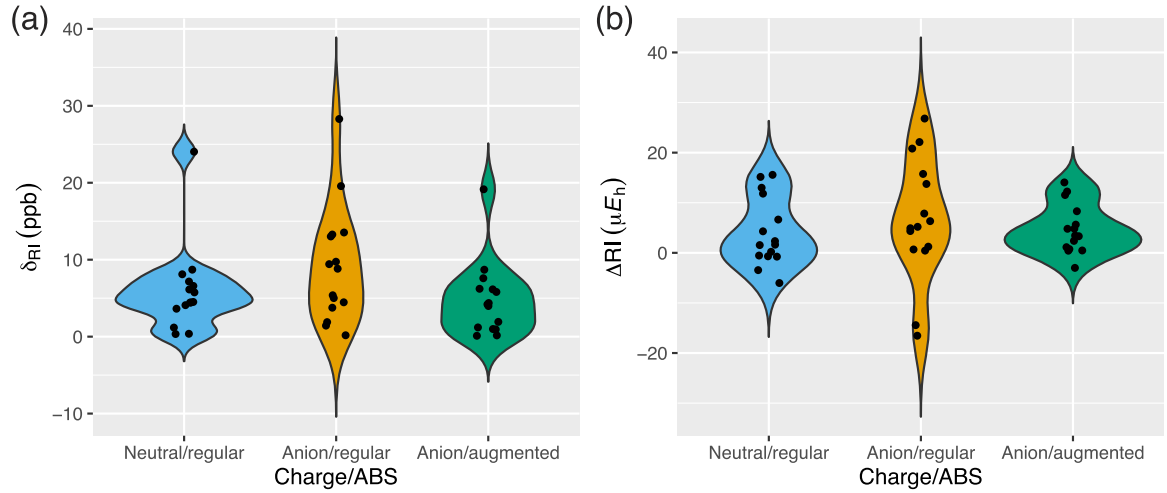

FIG. 1. Distribution of the errors in the RI approximation due to using OptRI auxiliary sets (relative to a large, even-tempered reference) with DZ quality basis sets for 15 heavy p-block elements. (a) Error in the multielectron integrals expressed through the δ_{RI} metric. (b) Error in the MP2-F12 correlation energy. Each panel shows three charge/ABS pairs, where the charge specifies the neutral atom or its anion, and the ABS is either the regular cc-pVDZ-PP-F12-OptRI or the newly developed augmented aug-cc-pVDZ-PP-F12-OptRI. Calculations on the neutral atom use the cc-pVDZ-PP-F12 OBS, while the aug-cc-pVDZ-PP-F12 OBS is used for the anion.

geminal Slater exponent of 1.0 a_0^{-1} at all zeta levels. Open-shell calculations were carried out using restricted open-shell Hartree–Fock (ROHF), with the spin-restriction relaxed in the CCSD component, which could be abbreviated as R/UCCSD(T)-F12b. To investigate the effect of the additional diffuse functions on the EAs of the heavy post-d elements, calculations were carried out with both the existing cc-pV*n*Z-PP-F12 and the newly developed aug-cc-pV*n*Z-PP-F12 families of OBSs and ABSs. The ABSs used in the fitting of the Coulomb and exchange integrals were def2-QZVPP-JKFit and def2-AQZVPP-JKFit, respectively. Unless otherwise stated, only the valence s and p electrons were correlated.

To establish CBS limits for EAs, a number of extrapolation formulae were used. For HF calculations, the two-point extrapolation of Karton and Martin is often used, which is given by

$$E_L^{\mathrm{HF}} = E_{\mathrm{CBS}}^{\mathrm{HF}} + A(L+1)\exp\left(-9\sqrt{L}\right), \tag{2}$$

where L is the highest angular symmetry present in the orbital basis set.[52] For lighter elements with conventional correlation consistent basis sets, $L+1$ would be equivalent to $n+1$, where n is the basis set cardinal number. However, this does not account for the F12 specific basis sets incorporating aug-cc-pV$(n+1)$Z functions for the lower angular symmetries and, hence, could potentially lead to CBS estimates that are too low in energy. To ensure a more conservative estimate of the HF CBS limit, it is proposed that $L+1$ in Eq. (2) can be replaced with $n+2$ when F12 specific basis sets are used [$(n+1)$ from the basis set construction, combined with the $(n+1)$ from the extrapolation], leading to

$$E_n^{\mathrm{HF}} = E_{\mathrm{CBS}}^{\mathrm{HF}} + A(n+2)\exp\left(-9\sqrt{n}\right). \tag{3}$$

The CABS singles correction is not used in this extrapolation. The HF limit can also be approximated by taking the HF energy evaluated with the largest available F12 specific basis set (aug-cc-pVQZ-PP-F12 in this case) and adding the CABS singles correction. The two approaches of using either Eq. (3) to extrapolate the aug-cc-pVTZ-PP-F12 and aug-cc-pVQZ-PP-F12 results [denoted CBS(T, Q) herein] or aug-cc-pVQZ-PP-F12 plus CABS correction (QZ + CABS) are briefly compared below.

Extrapolation of the CCSD-F12b and (T) correlation energies used the generalized two-point formula of Schwenke,

$$E_{\mathrm{CBS}}^{\mathrm{corr}} = \left(E_{\mathrm{large}}^{\mathrm{corr}} - E_{\mathrm{small}}^{\mathrm{corr}}\right)F + E_{\mathrm{small}}^{\mathrm{corr}}, \tag{4}$$

where, in principle, F can be any function or scalar value.[53] In this case, $E_{\mathrm{small}}^{\mathrm{corr}}$ and $E_{\mathrm{large}}^{\mathrm{corr}}$ are the correlation energy components evaluated with aug-cc-pVTZ-PP-F12 and aug-cc-pVQZ-PP-F12, respectively. The CCSD-F12b and (T) components are extrapolated separately, using $F = 1.363\,388$ and $F = 1.769\,474$, respectively.[12]

IV. RESULTS AND DISCUSSION

The electron affinities of Ga–Br, In–I, and Tl–At have previously been computed using a relativistic coupled-cluster version of the Feller–Peterson–Dixon (FPD)[54,55] composite method,[56,57] which included contributions from higher order correlation effects (CCSDTQ), Lamb shift quantum electrodynamics effects (QED), and spin–orbit (SO) coupling including the Gaunt contribution. The calculated values have a mean unsigned error of 0.20 kcal mol^{-1} relative to the experimental data available at the time, and the same work predicted theoretical best-estimates of the EAs for Po and At, which did not have experimental values. Subsequently, the EA of astatine has been measured,[58] and more accurate values for gallium and thallium have been determined.[59–61] In this work, the goal is not to revisit the effects of higher order correlation, SO

TABLE IV. Convergence of the HF energy (E_h) for the neutral ground-state of the 5p atoms In–Xe using the aV*n*Z-F12 basis sets. These basis sets are paired with the ECP28MDF pseudopotential.

Element	aVDZ-F12	aVTZ-F12	aVQZ-F12	CBS(T, Q)	QZ + CABS
In	−189.207 442	−189.207 561	−189.207 674	−189.207 688	−189.207 674
Sn	−213.336 538	−213.336 712	−213.336 845	−213.336 861	−213.336 845
Sb	−239.275 839	−239.275 995	−239.276 028	−239.276 032	−239.276 028
Te	−266.999 965	−267.001 653	−267.001 798	−267.001 815	−267.001 809
I	−294.656 091	−294.657 733	−294.657 945	−294.657 971	−294.657 964
Xe	−328.298 669	−328.299 143	−328.299 193	−328.299 199	−328.299 193

coupling, etc., but rather to investigate the performance of the aug-cc-pV*n*Z-PP-F12 basis sets developed in this work and their use in estimating CCSD(T) basis set limits. For this reason, the EAs are reported in kcal mol^{-1}, rather than eV.

Two methods for estimating the HF CBS limit using F12 specific basis sets are described in Sec. III: CBS(T, Q), which uses a CBS extrapolation formula, and QZ + CABS, which relies on the CABS singles correction. To first calibrate the performance of CBS(T, Q), estimates of the HF/CBS limit are calculated for the neutral ground-state atoms of the 18 heavy post-d elements and compared to the equivalent CBS limits estimated using Eq. (2) with the conventional aug-cc-pVQZ-PP and aug-cc-pV5Z-PP basis sets. The mean unsigned deviation between these two estimates is 17 μE_h, with a mean signed deviation of $-10\mu E_h$, where the negative sign indicates that the CBS(T, Q) estimate produces a lower energy value. The excellent agreement between the conventional and F12 basis set specific extrapolation methods suggests that CBS(T, Q) is producing reasonable estimates of the CBS limits, and as it tends to produce a slightly lower energy, the modifications in Eq. (3) to produce a more conservative estimate are vindicated.

With CBS(T, Q) established as a reasonable methodology for estimating HF/CBS limits of these neutral atoms, Table IV shows a comparison of this CBS(T, Q) approach with the simpler QZ + CABS for the 5p atoms In–Xe, where it can be seen that CBS(T, Q) always produces a slightly lower energy with a mean deviation between the two estimates of $-9\mu E_h$. The table also shows the convergence of the HF energy with respect to basis set cardinal number, where it can be seen that for In and Sn, the improvement in the HF energy is roughly linear, presumably due to changes in energy between successive basis set cardinal numbers being small even at the DZ to TZ level. This suggests that the CBS estimates for these two elements may be slightly too conservative. For the other elements considered, the energy appears to be rapidly converging toward a limiting value, with a relative large change from DZ to TZ and a small change from TZ to QZ. Comparing the QZ + CABS data in Table IV with that for aVQZ-F12 indicates that the CABS singles correction is very small, clearly less than 1 μE_h for In, Sn, Sb, and Xe. As the CABS correction is small, and there is little deviation between CBS(T, Q) and QZ + CABS, CBS(T, Q) is used for estimating HF CBS limits herein.

The CCSD(T)-F12b/aV*n*Z-F12 electron affinities for the heavy p-block elements Ga–Br, In–I, and Tl–At are given in Table V, along with a CBS estimate based on using CBS(T, Q) for the HF energies and Eq. (4) for the correlation contributions. Also shown (in parentheses) is the effect of the additional diffuse higher angular momentum functions, evaluated as the difference in the EA with the aV*n*Z-F12 orbital basis compared to the analogous V*n*Z-F12 basis. Unsurprisingly, the additional diffuse functions always produce EAs that are closer to CBS estimates, and the general trend is that the effect of the diffuse functions is largest at the DZ level, reduces through TZ, and is smallest at QZ. However, for the 6p elements Tl–At, the effect is slightly larger at the TZ level than at DZ or QZ. In all cases, the EA converges rapidly toward the estimated CBS limit, with the difference between aVQZ-F12 and CBS in the range of 0.02–0.06 kcal mol^{-1} per correlated electron.

The convergence of the EAs for Ga, Te, and Bi is also shown graphically in Fig. 2, where the explicitly correlated CCSD(T)-F12b results with the aV*n*Z-F12 and V*n*Z-F12 basis set families are also compared to the conventional CCSD(T)/aug-cc-pV*n*Z-PP[31,62] [denoted aV*n*Z (conv)] values. For Ga, where the basis set effect on EA is small, it can be seen that explicit correlation with the existing V*n*Z-F12 basis sets holds almost no advantage over conventional results at the same zeta-level. The addition of the higher angular momentum diffuse functions improves the F12 results, and this

TABLE V. Convergence of CCSD(T)-F12b electron affinities (kcal mol^{-1}) with respect to orbital basis set. Values in parentheses indicate the change relative to using the analogous V*n*Z-F12 orbital basis set.

Element	aVDZ-F12	aVTZ-F12	aVQZ-F12	CBS
Ga	6.92 (0.43)	7.59 (0.26)	7.65 (0.12)	7.71
Ge	29.82 (0.32)	30.95 (0.17)	31.05 (0.07)	31.15
As	13.54 (0.56)	16.22 (0.28)	16.80 (0.14)	17.06
Se	44.48 (0.44)	46.26 (0.20)	46.96 (0.09)	47.28
Br	79.14 (0.38)	79.69 (0.15)	80.49 (0.09)	80.84
In	9.16 (0.30)	9.93 (0.19)	10.00 (0.12)	10.05
Sn	31.12 (0.19)	32.42 (0.13)	32.52 (0.05)	32.62
Sb	16.87 (0.38)	19.95 (0.26)	20.64 (0.21)	20.94
Te	44.67 (0.38)	46.75 (0.26)	47.57 (0.16)	47.95
I	75.02 (0.30)	75.59 (0.21)	76.51 (0.18)	76.94
Tl	6.74 (0.33)	7.35 (0.46)	7.37 (0.24)	7.42
Pb	28.43 (0.20)	29.47 (0.35)	29.49 (0.15)	29.57
Bi	14.91 (0.36)	17.75 (0.62)	18.42 (0.32)	18.71
Po	41.66 (0.25)	43.59 (0.43)	44.33 (0.21)	44.68
At	70.60 (0.19)	71.16 (0.36)	71.97 (0.18)	72.36

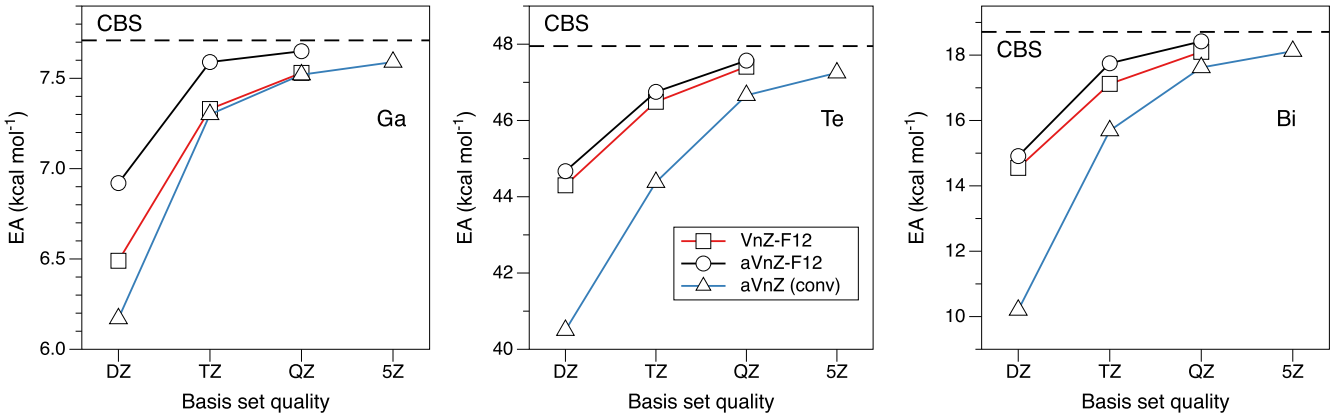

FIG. 2. Convergence of the CCSD(T) electron affinities for Ga, Te, and Bi using conventional CCSD(T) [aV*n*Z (conv)] and explicitly correlated CCSD(T)-F12b (new aV*n*Z-F12 and existing V*n*Z-F12). The estimated CBS limits are shown as horizontal dashed lines and were obtained by extrapolation of the aV*n*Z-F12 results with n = T, Q.

is particularly striking at the TZ level, where the F12 EA is the same as the conventional aV5Z result. For Te and Bi, the effect of using F12 is more apparent, even with the existing V*n*Z-F12 sets, but it is still clear that the additional diffuse functions included in aV*n*Z-F12 produce EAs closer to the CBS limit and that CCSD(T)-F12b/aV*n*Z-F12 rapidly approaches the estimated CBS limit. It was noted above that the EAs of the 6p elements are significantly improved by additional functions at the TZ level, and this can be seen for Bi in Fig. 2 (right panel), where the overall effect is a smoother and quicker convergence toward the CBS limit. The improvement in convergence with respect to basis set shown in Fig. 2 indicates that the estimated CBS limits from this work, based on explicitly correlated energies, are likely to be an improvement over those based on extrapolations of conventional CCSD(T) energies with aug-cc-pV*n*Z-PP (n = Q, 5) basis sets.

Table VI shows a comparison of the CBS estimates for the EAs of the heavy p-block elements from two different approaches: the CBS(T, Q) approach based on F12 methods used in this work and the estimates of Finney and Peterson based on conventional CCSD(T) with aug-cc-pwCV*n*Z-PP (n = Q, 5) basis sets.[56] In the latter, the HF energies were extrapolated using Eq. (2) (replacing L with the basis set cardinal number n), and the extrapolated frozen-core CCSD(T) correlation energies were produced using the formula of Martin as follows:[74]

$$E_n^{\mathrm{corr}} = E_{\mathrm{CBS}}^{\mathrm{corr}} + \frac{B}{(n+1/2)^4}.$$

It can be seen that the CBS limits of this work are consistently larger than those of Finney and Peterson, although the difference is small with a mean average of 0.15 kcal mol^{-1} and the largest deviation occurring for iodine (0.26 kcal mol^{-1}). Perhaps more significantly, a comparison of Table V with Table VI highlights that, for the group 13 and 14 elements considered, CCSD(T)-F12b/aVQZ-F12 computes EAs that are beyond the CBS estimates of Finney and Peterson, suggesting that the latter are underestimates of the true CBS limit. This adds additional justification to the revised CBS estimates of this work.

The combined post-frozen-core CCSD(T) contributions to EAs from the additive FPD approach, previously published by Finney and Peterson (ΔFPD),[56,57] are also reproduced in Table VI. This includes correlation of outer-core electrons, a correction for using scalar relativistic PPs, higher order correlation effects, QED effects, and SO coupling. These individual contributions are analyzed in detail in the work of Finney and Peterson and have been combined into a single value here for convenience. The SO contribution dominates ΔFPD,[57] but it is interesting to note that the improvements to the frozen-core CBS estimates in this work are of the same magnitude as the corrections for using PPs, higher order correlation effects, or QED. In the case of thallium, the difference between the two CBS estimates is greater than the total ΔFPD, but this reflects

TABLE VI. Comparison of CBS estimates of electron affinities (kcal mol^{-1}) from conventional CCSD(T) (Finney) and CCSD(T)-F12b (this work). A total of additive contributions from the FPD composite method (ΔFPD) taken from Ref. 57 are added to the CBS estimate from this work to produce revised final FPD values.

Element	CBS (Ref. 56)	CBS (this work)	ΔFPD[57]	Revised final FPD	Expt.
Ga	7.64	7.71	−0.67	7.04	6.95[59]
Ge	31.03	31.15	−2.38	28.77	28.43[63]
As	16.93	17.06	+1.47	18.53	18.54[64]
Se	47.08	47.28	−0.51	46.77	46.60[65]
Br	80.59	80.84	−3.08	77.76	77.57[66]
In	9.98	10.05	−1.07	8.98	8.85[67]
Sn	32.49	32.62	−6.23	26.39	25.64[68]
Sb	20.84	20.94	+3.22	24.16	24.15[69]
Te	47.77	47.95	−2.19	45.76	45.45[70]
I	76.68	76.94	−6.12	70.82	70.54[71]
Tl	7.36	7.42	+0.03	7.45	7.38[61]
Pb	29.46	29.57	−20.95	8.62	8.23[72]
Bi	18.58	18.71	+3.86	22.57	21.73[73]
Po	44.51	44.68	−10.30	34.38	⋯
At	72.15	72.36	−16.32	56.04	55.71[58]

the fortuitous cancellation of post-frozen-core CCSD(T) effects for the EA of this element.

The penultimate column of Table VI reports revised final FPD values that have been constructed by summing the CBS estimates from this work with the ΔFPD of Finney and Peterson. Due to the small nature of the revisions to these FPD EAs, the conclusions of Finney and Peterson would be largely unchanged, although the uncertainty in the final values due to the frozen-core CBS estimate would be slightly reduced. Table VI also summarizes the available experimental EAs. For Ga, Tl, and At, where accurate experimental values have been determined since the work of Finney and Peterson,[58–61] the agreement between the revised FPD data of this work and experiment is excellent, matching the trends for the other elements investigated.

There remains a question of how important are the higher angular momentum diffuse functions developed in this work to the EAs of the heavy p-block elements. While the overall effect of including these functions is displayed in Tables V, it is interesting to place the magnitude of this change into context with the effect of post-frozen-core CCSD(T) contributions. Outside of SO effects, the largest FPD contribution to the EAs is correlation of outer-core electrons;[56] hence, Table VII shows a comparison of the effect of augmenting with higher angular momentum diffuse functions (Δaug) with the effect of correlating the $(m-1)$d electrons (Δd). This Δd is evaluated as the difference between the EAs with $m$sp + $(m-1)$d electrons correlated and those with only the $m$sp valence electrons correlated. In both cases, the newly developed aug-cc-pVnZ-PP-F12 orbital and auxiliary basis sets are used with a geminal Slater exponent of 1.0 a_0^{-1}. Calculations with separate geminal exponents for the valence and outer-core electrons were not tested in this case but would be likely to yield further improvements.[75] A comparison of the absolute values of Δaug and Δd for any given basis set shows that these two contributions to the EA are of roughly the same magnitude; hence, the addition of higher angular momentum diffuse functions is of the same importance as accounting for the correlation of $(m-1)$d electrons.

Focusing momentarily on the convergence of Δd with respect to basis set size, it can be seen in Table VII that convergence appears to be rapid, with the TZ results close to those from QZ. As expected, there is a larger, although still relatively small, difference between Δd at the DZ level and the same quantity evaluated with the TZ basis. In some cases, namely As, Sn, and Tl, the Δd contribution changes sign between DZ and TZ, indicating that Δd should be evaluated at the TZ level or better. It is also noted that the QZ Δd contribution of Table VII is very close to the ΔCV values reported by Finney and Peterson,[56] with a mean absolute deviation of 0.06 kcal mol^{-1} and a maximum deviation of 0.12 kcal mol^{-1}. The ΔCV values are based on extrapolations to the CCSD(T)/CBS limit using aug-cc-pwCVnZ-PP (n = Q, 5) basis sets with all electrons not replaced by the PP correlated; hence, these also correlate the $(m-1)$sp electrons along with $(m-1)$d. Overall, the rapid convergence of Δd and the excellent agreement with ΔCV reinforce the finding that F12 methods with the (aug-)cc-pVnZ-PP-F12 family of basis sets are an efficient way of recovering this important correlation effect.[26]

TABLE VII. Effect on the CCSD(T)-F12b EAs (kcal mol^{-1}) of the heavy p-block elements at each basis set zeta-level from augmentation with additional higher angular momentum diffuse functions (Δaug) and from correlation of $(m-1)$d electrons (Δd).

	DZ		TZ		QZ	
Element	Δaug	Δd	Δaug	Δd	Δaug	Δd
Ga	+0.43	−0.38	+0.26	−0.26	+0.12	−0.31
Ge	+0.32	+0.03	+0.17	+0.11	+0.07	+0.07
As	+0.56	+0.17	+0.28	−0.01	+0.14	−0.12
Se	+0.44	+0.23	+0.20	+0.13	+0.09	+0.04
Br	+0.38	+0.18	+0.15	+0.15	+0.09	+0.11
In	+0.30	−0.57	+0.19	−0.33	+0.12	−0.30
Sn	+0.19	−0.07	+0.13	+0.12	+0.05	+0.18
Sb	+0.38	+0.27	+0.26	+0.17	+0.21	+0.01
Te	+0.38	+0.34	+0.26	+0.39	+0.16	+0.26
I	+0.30	+0.31	+0.21	+0.42	+0.18	+0.39
Tl	+0.33	−0.12	+0.46	+0.22	+0.24	+0.34
Pb	+0.20	+0.32	+0.35	+0.64	+0.15	+0.82
Bi	+0.36	+0.70	+0.62	+0.65	+0.32	+0.51
Po	+0.25	+0.67	+0.43	+0.84	+0.21	+0.77
At	+0.19	+0.49	+0.36	+0.83	+0.18	+0.83

V. CONCLUSIONS

New higher angular momentum diffuse functions have been developed for augmenting the cc-pVnZ-PP-F12 (n = D, T, Q) basis sets for the heavy p-block elements Ga–Kr, In–Xe, and Tl–Rn, to be used in explicitly correlated electronic structure calculations. Following the established correlation consistent basis naming convention, these new sets are denoted aug-cc-pVnZ-PP-F12. In addition to orbital basis sets, matching auxiliary basis sets for use in the density fitting of two-electron repulsion integrals (MP2Fit) and complementary auxiliary basis sets for the RI in F12 methods (OptRI) have also been developed. Benchmark calculations of electron affinities at the CCSD(T)-F12b level of theory with the new basis sets demonstrates the importance of the additional diffuse functions, leading to an improvement in convergence toward the complete basis set limit. To produce revised CBS estimates of the EA, a minor modification of the HF two-point extrapolation of Karton and Martin is proposed, which takes account of the additional s-, p-, and d-type functions in the F12 specific basis sets for these elements.[26,52] When combined with a Schwenke-type extrapolation of correlation energy, this leads to slightly greater CBS estimates of the frozen-core CCSD(T) electron affinities compared to those from previously published conventional CCSD(T) results. These new CBS estimates were then combined with the composite ΔFPD contribution of Finney and Peterson to produce revised theoretical "best-estimates" of the EAs. It was found that the new higher angular momentum diffuse functions are approximately as important to the EA as the correlation of outer-core electrons, which is the biggest post-frozen-core CCSD(T) contribution outside of spin–orbit coupling effects.[56]

All of the basis sets developed in this work are provided in machine readable format in the supplementary material. They will also be made available for download from the online repository of correlation consistent basis sets (ccRepo)[76] and incorporated into the Molpro basis set library.

SUPPLEMENTARY MATERIAL

See the supplementary material for the exponents of the basis sets developed in this work, both orbital and auxiliary, in Molpro format. Also included are the absolute energies of the neutral atoms and anions used in the calculation of the electron affinities and details on the interpolation formulae, and the resulting exponents for the noble gas elements, along with further data used to determine the process to augment the MP2Fit auxiliary sets with additional diffuse functions. The final composition of the OptRI auxiliary sets and the violin plots demonstrating their performance at the TZ and QZ levels are also provided in the supplementary material.

ACKNOWLEDGMENTS

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

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

J. Grant Hill: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

REFERENCES

[1]S. Ten-no and J. Noga, "Explicitly correlated electronic structure theory from R12/F12 ansätze," WIREs Comput. Mol. Sci. **2**, 114 (2012).
[2]C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, "Explicitly correlated electrons in molecules," Chem. Rev. **112**, 4 (2012).
[3]L. Kong, F. A. Bischoff, and E. F. Valeev, "Explicitly correlated R12/F12 methods for electronic structure," Chem. Rev. **112**, 75 (2012).
[4]R. J. Bartlett and M. Musiał, "Coupled-cluster theory in quantum chemistry," Rev. Mod. Phys. **79**, 291 (2007).
[5]T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," J. Chem. Phys. **90**, 1007 (1989).
[6]A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, "Basis-set convergence in correlated calculations on Ne, N_2, and H_2O," Chem. Phys. Lett. **286**, 243 (1998).
[7]D. Feller, K. A. Peterson, and J. Grant Hill, "On the effectiveness of CCSD(T) complete basis set extrapolations for atomization energies," J. Chem. Phys. **135**, 044102 (2011).
[8]D. S. Ranasinghe and G. A. Petersson, "CCSD(T)/CBS atomic and molecular benchmarks for H through Ar," J. Chem. Phys. **138**, 144104 (2013).
[9]T. Shiozaki and H.-J. Werner, "Multireference explicitly correlated F12 theories," Mol. Phys. **111**, 607 (2013).
[10]D. P. Tew, W. Klopper, C. Neiss, and C. Hättig, "Quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets," Phys. Chem. Chem. Phys. **9**, 1921 (2007).
[11]F. A. Bischoff, S. Wolfsegger, D. P. Tew, and W. Klopper, "Assessment of basis sets for F12 explicitly-correlated molecular electronic-structure methods," Mol. Phys. **107**, 963 (2009).
[12]J. G. Hill, K. A. Peterson, G. Knizia, and H.-J. Werner, "Extrapolating MP2 and CCSD explicitly correlated correlation energies to the complete basis set limit with first and second row correlation consistent basis sets," J. Chem. Phys. **131**, 194105 (2009).
[13]B. Brauer, M. K. Kesharwani, S. Kozuch, and J. M. L. Martin, "The S66x8 benchmark for noncovalent interactions revisited: explicitly correlated *ab initio* methods and density functional theory," Phys. Chem. Chem. Phys. **18**, 20905 (2016).
[14]N. Mehta and J. M. L. Martin, "MP2-F12 basis set convergence near the complete basis set limit: are *h* functions sufficient?," J. Phys. Chem. A **126**, 3964 (2022).
[15]O. Vahtras, J. Almlöf, and M. W. Feyereisen, "Integral approximations for LCAO-SCF calculations," Chem. Phys. Lett. **213**, 514 (1993).
[16]M. W. Feyereisen, G. Fitzgerald, and A. Komornicki, "Use of approximate integrals in ab initio theory. An application in MP2 energy calculations," Chem. Phys. Lett. **208**, 359 (1993).
[17]F. Weigend, "A fully direct RI-HF algorithm: Implementation, optimised auxiliary basis sets, demonstration of accuracy and efficiency," Phys. Chem. Chem. Phys. **4**, 4285 (2002).
[18]W. Kutzelnigg, "r_{12}-Dependent terms in the wave function as closed sums of partial wave amplitudes for large l," Theor. Chim. Acta **68**, 445 (1985).
[19]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, "The Molpro quantum chemistry package," J. Chem. Phys. **152**, 144107 (2020).
[20]H.-J. Werner, P. J. Knowles, P. Celani, W. Györffy, A. Hesselmann, D. Kats, G. Knizia, A. Köhn, T. Korona, D. Kreplin, R. Lindh, Q. Ma, F. R. Manby, A. Mitrushenkov, G. Rauhut, M. Schütz, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, J. A. Black, P. J. Bygrave, R. Cimiraglia, D. L. Cooper, D. Coughtrie, M. J. O. Deegan, A. J. Dobbyn, K. Doll, M. Dornbach, F. Eckert, S. Erfort, E. Goll, C. Hampel, G. Hetzer, J. G. Hill, M. Hodges, T. Hrenar, G. Jansen, C. Köppl, C. Kollmar, S. J. R. Lee, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, B. Mussard, S. J. McNicholas, W. Meyer, T. F. Miller III, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. A. Peterson, K. Pflüger, R. Pitzer, I. Polyak, M. Reiher, J. O. Richardson, J. B. Robinson, B. Schröder, M. Schwilk, T. Shiozaki, M. Sibaev, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, J. Toulouse, M. Wang, M. Welborn, and B. Ziegler, *MOLPRO, version 2023.1, a package of ab initio programs*, see http://www.molpro.net (2023).
[21]A. J. May and F. R. Manby, "An explicitly correlated second order Møller-Plesset theory using a frozen Gaussian geminal," J. Chem. Phys. **121**, 4479 (2004).
[22]J. G. Hill, S. Mazumder, and K. A. Peterson, "Correlation consistent basis sets for molecular core-valence effects with explicitly correlated wave functions: The atoms B–Ne and Al–Ar," J. Chem. Phys. **132**, 054108 (2010).
[23]K. A. Peterson, T. B. Adler, and H.-J. Werner, "Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B–Ne, and Al–Ar," J. Chem. Phys. **128**, 084102 (2008).
[24]K. A. Peterson, M. K. Kesharwani, and J. M. L. Martin, "The cc-pV5Z-F12 basis set: reaching the basis set limit in explicitly correlated calculations," Mol. Phys. **113**, 1551 (2015).
[25]J. G. Hill and K. A. Peterson, "Correlation consistent basis sets for explicitly correlated wavefunctions: valence and core–valence basis sets for Li, Be, Na, and Mg," Phys. Chem. Chem. Phys. **12**, 10460 (2010).
[26]J. G. Hill and K. A. Peterson, "Correlation consistent basis sets for explicitly correlated wavefunctions: Pseudopotential-based basis sets for the post-d main group elements Ga–Rn," J. Chem. Phys. **141**, 094106 (2014).
[27]J. G. Hill and R. A. Shaw, "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," J. Chem. Phys. **155**, 174113 (2021).

[28]R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," J. Chem. Phys. **96**, 6796 (1992).
[29]B. Metz, M. Schweizer, H. Stoll, M. Dolg, and W. Liu, Theor. Chem. Acc. **104**, 22 (2000).
[30]B. Metz, H. Stoll, and M. Dolg, J. Chem. Phys. **113**, 2563 (2000).
[31]K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, "Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-*d* group 16–18 elements," J. Chem. Phys. **119**, 11113 (2003).
[32]K. A. Peterson, B. C. Shepler, D. Figgen, and H. Stoll, "On the spectroscopic and thermochemical properties of ClO, BrO, IO, and their anions," J. Phys. Chem. A **110**, 13877 (2006).
[33]N. Sylvetsky, M. K. Kesharwani, and J. M. L. Martin, "The aug-cc-pVnZ-F12 basis set family: Correlation consistent basis sets for explicitly correlated benchmark calculations on anions and noncovalent complexes," J. Chem. Phys. **147**, 134106 (2017).
[34]J. A. Nelder and R. Mead, "A simplex method for function minimization," Comput. J. **7**, 308 (1965).
[35]F. Weigend, "Hartree–Fock exchange fitting basis sets for H to Rn," J. Comput. Chem. **29**, 167 (2008).
[36]H.-J. Werner, T. B. Adler, and F. R. Manby, "General orbital invariant MP2-F12 theory," J. Chem. Phys. **126**, 164102 (2007).
[37]F. Weigend, A. Köhn, and C. Hättig, "Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations," J. Chem. Phys. **116**, 3175 (2002).
[38]C. Hättig, G. Schmitz, and J. Koßmann, "Auxiliary basis sets for density-fitted correlated wavefunction calculations: Weighted core-valence and ECP basis sets for post-d elements," Phys. Chem. Chem. Phys. **14**, 6549 (2012).
[39]F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, "RI-MP2: optimized auxiliary basis sets and demonstration of efficiency," Chem. Phys. Lett. **294**, 143 (1998).
[40]C. Hättig and F. Weigend, "CC2 excitation energy calculations on large molecules using the resolution of the identity approximation," J. Chem. Phys. **113**, 5154 (2000).
[41]C. Hättig, "Geometry optimizations with the coupled-cluster model CC2 using the resolution-of-the-identity approximation," J. Chem. Phys. **118**, 7751 (2003).
[42]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, "TURBOMOLE: Modular program suite for *ab initio* quantum-chemical and condensed-matter simulations," J. Chem. Phys. **152**, 184107 (2020).
[43]TURBOMOLE V7.0.2 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[44]C. Hättig, "Optimization of auxiliary basis sets for RI-MP2 and RI-CC2 calculations: Core-valence and quintuple-ζ basis sets for H to Ar and QZVPP basis sets for Li to Kr," Phys. Chem. Chem. Phys. **7**, 59 (2005).
[45]E. F. Valeev, "Improving on the resolution of the identity in linear R12 ab initio theories," Chem. Phys. Lett. **395**, 190 (2004).
[46]K. E. Yousaf and K. A. Peterson, "Optimized auxiliary basis sets for explicitly correlated methods," J. Chem. Phys. **129**, 184108 (2008).
[47]R. A. Shaw and J. G. Hill, "Approaching the Hartree–Fock limit through the complementary auxiliary basis set singles correction and auxiliary basis sets," J. Chem. Theory Comput. **13**, 1691 (2017).
[48]T. B. Adler, G. Knizia, and H.-J. Werner, "A simple and efficient CCSD(T)-F12 approximation," J. Chem. Phys. **127**, 221106 (2007).
[49]G. Knizia and H.-J. Werner, "Explicitly correlated RMP2 for high-spin open-shell reference states," J. Chem. Phys. **128**, 154103 (2008).
[50]G. Knizia, T. B. Adler, and H.-J. Werner, "Simplified CCSD(T)-F12 methods: Theory and benchmarks," J. Chem. Phys. **130**, 054104 (2009).
[51]S. Ten-No, "Initiation of explicitly correlated Slater-type geminal theory," Chem. Phys. Lett. **398**, 56 (2004).
[52]A. Karton and J. M. L. Martin, "Comment on: 'Estimating the Hartree–Fock limit from finite basis set calculations,'" Theor. Chem. Acc. **115**, 330 (2006).
[53]D. W. Schwenke, "The extrapolation of one-electron basis sets in electronic structure calculations: How it should work and how it can be made to work," J. Chem. Phys. **122**, 014107 (2005).
[54]D. Feller, K. A. Peterson, and D. A. Dixon, "A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures," J. Chem. Phys. **129**, 204105 (2008).
[55]D. Feller, K. A. Peterson, and D. A. Dixon, "Further benchmarks of a composite, convergent, statistically calibrated coupled-cluster-based approach for thermochemical and spectroscopic studies," Mol. Phys. **110**, 2381 (2012).
[56]B. A. Finney and K. A. Peterson, "Beyond chemical accuracy in the heavy p-block: The first ionization potentials and electron affinities of Ga–Kr, In–Xe, and Tl–Rn," J. Chem. Phys. **151**, 024303 (2019).
[57]B. A. Finney and K. A. Peterson, "Erratum: 'Beyond chemical accuracy in the heavy p-block: The first ionization potentials and electron affinities of Ga–Kr, In–Xe, and Tl–Rn,'" J. Chem. Phys. **151**, 159901 (2019).
[58]D. Leimbach, J. Karls, Y. Guo, R. Ahmed, J. Ballof, L. Bengtsson, F. Boix Pamies, A. Borschevsky, K. Chrysalidis, E. Eliav, D. Fedorov, V. Fedosseev, O. Forstner, N. Galland, R. F. Garcia Ruiz, C. Granados, R. Heinke, K. Johnston, A. Koszorus, U. Köster, M. K. Kristiansson, Y. Liu, B. Marsh, P. Molkanov, L. F. Pašteka, J. P. Ramos, E. Renault, M. Reponen, A. Ringvall-Moberg, R. E. Rossel, D. Studer, A. Vernon, J. Warbinek, J. Welander, K. Wendt, S. Wilkins, D. Hanstorp, and S. Rothe, "The electron affinity of astatine," Nat. Commun. **11**, 3824 (2020).
[59]N. D. Gibson, C. W. Walter, C. Crocker, J. Wang, W. Nakayama, J. N. Yukich, E. Eliav, and U. Kaldor, "Electron affinity of gallium and fine structure of Ga^-: Experiment and theory," Phys. Rev. A **100**, 052512 (2019).
[60]R. Tang, X. Fu, Y. Lu, and C. Ning, "Accurate electron affinity of Ga and fine structures of its anions," J. Chem. Phys. **152**, 114303 (2020).
[61]C. W. Walter, N. D. Gibson, and S. E. Spielman, "Electron affinity of thallium measured with threshold spectroscopy," Phys. Rev. A **101**, 052511 (2020).
[62]K. A. Peterson, "Systematically convergent basis sets with relativistic pseudopotentials. I. Correlation consistent basis sets for the post-*d* group 13–15 elements," J. Chem. Phys. **119**, 11099 (2003).
[63]D. Bresteau, P. Babilotte, C. Drag, and C. Blondel, "Intra-cavity photodetachment microscopy and the electron affinity of germanium," J. Phys. B: At., Mol. Opt. Phys. **48**, 125001 (2015).
[64]C. W. Walter, N. D. Gibson, R. L. Field III, A. P. Snedden, J. Z. Shapiro, C. M. Janczak, and D. Hanstorp, "Electron affinity of arsenic and the fine structure of As^- measured using infrared photodetachment threshold spectroscopy," Phys. Rev. A **80**, 014501 (2009).
[65]M. Vandevraye, C. Drag, and C. Blondel, "Electron affinity of selenium measured by photodetachment microscopy," Phys. Rev. A **85**, 015401 (2012).
[66]C. Blondel, P. Cacciani, C. Delsart, and R. Trainham, "High-resolution determination of the electron affinity of fluorine and bromine using crossed ion and laser beams," Phys. Rev. A **40**, 3698 (1989).
[67]C. W. Walter, N. D. Gibson, D. J. Carman, Y. Li, and D. J. Matyas, "Electron affinity of indium and the fine structure of In^- measured using infrared photodetachment threshold spectroscopy," Phys. Rev. A **82**, 032507 (2010).
[68]M. Vandevraye, C. Drag, and C. Blondel, "Electron affinity of tin measured by photodetachment microscopy," J. Phys. B: At., Mol. Opt. Phys. **46**, 125002 (2013).
[69]M. Scheer, H. K. Haugen, and D. R. Beck, "Single- and multiphoton infrared laser spectroscopy of Sb^-: A case study," Phys. Rev. Lett. **79**, 4104 (1997).
[70]G. Haeffler, A. E. Klinkmüller, J. Rangell, U. Berzinsh, D. Hanstorp, and Z. PhysD - Atoms, "The electron affinity of tellurium," Z. Phys. D: At., Mol. Clusters **38**, 211 (1996).
[71]R. J. Peláez, C. Blondel, C. Delsart, and C. Drag, "Pulsed photodetachment microscopy and the electron affinity of iodine," J. Phys. B: At., Mol. Opt. Phys. **42**, 125001 (2009).
[72]X. Chen and C. Ning, "Accurate electron affinity of Pb and isotope shifts of binding energies of Pb^-," J. Chem. Phys. **145**, 084303 (2016).

[73]R. C. Bilodeau and H. K. Haugen, "Electron affinity of Bi using infrared laser photodetachment threshold spectroscopy," Phys. Rev. A **64**, 024501 (2001).
[74]J. M. L. Martin, "Ab initio total atomization energies of small molecules—Towards the basis set limit," Chem. Phys. Lett. **259**, 669 (1996).
[75]K. A. Peterson, C. Krause, H. Stoll, J. G. Hill, and H.-J. Werner, "Application of explicitly correlated coupled-cluster methods to molecules containing post-3*d* main group elements," Mol. Phys. **109**, 2607 (2011).
[76]ccRepo: A correlation consistent basis sets repository, http://www.grant-hill.group.shef.ac.uk/ccrepo/ (accessed 8 March 2024).