

Beyond chemical accuracy in the heavy p-block: The first ionization potentials and electron affinities of Ga-Kr, In-Xe, and Tl-Rn

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Abstract

A relativistic coupled-cluster version of the Feller-Peterson-Dixon (FPD) composite method has been used to accurately calculate the first ionization potentials (IP) and electron affinities (EAs) of the post-d, p-block elements Ga–Rn. Complete basis set (CBS) extrapolations including outer-core correlation at the CCSD(T) level of theory were combined with contributions from higher order electron correlation up to CCSDTQ, quantum electrodynamic effects (Lamb shift), and spin-orbit (SO) coupling including the Gaunt contribution. Several methods for including SO were investigated, in which all involved the four-component (4c) Dirac-Coulomb (DC) Hamiltonian. The treatment of SO coupling was the contribution that limited the final accuracy of the present results. In the cases where 4c-DC-CCSD(T) could be reliably used for the SO contributions, the final composite IPs and EAs agreed with the available experimental values to within an unsigned average error of just 0.16 and 0.20 kcal/mol, respectively. In all cases the final IPs and EAs were within 1 kcal/mol of the available experimental values, except for the EAs of the group 13 elements (Ga, In, Tl), where the currently accepted experimental values appear to be too large by as much as 4 kcal/mol. The values predicted in this work, which have estimated uncertainties of ± 0.5 kcal/mol, are 5.25 (Ga), 7.69 (In), and 7.39 (Tl) kcal/mol. For the EAs of Po and At, which do not have experimental values, the current calculations predict values of 34.2 and 55.8 kcal/mol with estimated uncertainties of ± 0.6 and ± 0.3 kcal/mol, respectively.

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I. INTRODUCTION

Ab initio thermochemistry calculations, particularly those employing composite methodologies based on coupled cluster expansions for electron correlation, have demonstrated accuracies for atomization enthalpies and heats of formation in the kJ/mol or even sub-kJ/mol range in the case of molecules containing elements in the first few rows of the periodic table.¹ For heavier elements, relativistic effects become much more important, and while the contributions of scalar relativity are straightforward to accurately include by using either the Douglas-Kroll-Hess (DKH)²⁻⁴ or exact 2-component (X2C) spin-free Hamiltonians,^{5,6} including the effects of spin-orbit (SO) coupling can be much more challenging. While its importance is often noted when working with the transition metals and of course the *f*-block lanthanides and actinides, it is sometimes neglected in the heavier p-block elements. Of course, even in molecules containing the lighter 2p and 3p elements, atomic SO is required to describe physical and chemical properties at or beyond chemical accuracy (~ 1 kcal/mol)⁷⁻¹⁰. When dealing with molecules containing the 4p elements and below, the inclusion of SO is mandatory for the accurate calculation of nearly any thermochemical property¹¹⁻¹⁴.

Ionization potentials (IP) and electron affinities (EA) are some of the most fundamental physical properties of atoms and molecules. For the 18 elements of the heavy (post-d) p-block, the first IPs for all of these elements have been accurately determined by experiment.¹⁵⁻³² Experimental values are also available for the EAs of Ga-Kr and In-Xe,³³⁻⁴² as well as those for Tl⁴³, Pb⁴⁴, and Bi⁴⁵ in the 6p period. The electron affinities of Po and At are currently not available from experiment, and the most commonly cited values of 44 ± 7 and 65 ± 5 kcal/mol, respectively, arise from the semiempirical extrapolations of Zollweg.⁴⁶ However, recent coupled cluster relativistic calculations of Borschevsky et al.⁴⁷ put the EA of Po at 33.9 kcal/mol and the EA of At at 55.6 kcal/mol. Some of the same authors, using a similar relativistic coupled cluster-based methodology, provided a theoretical value for the IP of At of 214.62 ± 0.58 kcal/mol that was in excellent agreement with the spectroscopic measurement reported in the same work of 214.87 kcal/mol.³¹ Presumably, their theoretical values for the EAs of Po and At should be considered far more reliable than the previous extrapolated results commonly used.

Debate however also exists over the reported experimental results are for Ga and Tl. The accepted experimental value for the EA of Ga is 9.91 ± 0.69 kcal/mol,³³ although the SO fine-structure was not resolved in the experiment. Theoretical calculations have predicted much lower

electron affinities of 6.94 and 7.03 kcal/mol using relativistic coupled-cluster singles and doubles (CCSD)⁴⁸ and multiconfigurational Dirac-Fock (MCDF)⁴⁹ methods, respectively. For the EA of Tl, the experimentally measured EA of Carpenter⁴³ is 8.69 ± 0.30 kcal/mol. This was in excellent agreement with the later relativistic CCSD calculations of Eliav et al.,⁴⁸ which yielded an EA of 9.22 ± 1.15 kcal/mol. However previous calculations using the multireference configuration interaction singles and doubles (MR-CISD) and MCDF methods predicted EAs of 6.23 kcal/mol⁵⁰ and 6.71 kcal/mol,⁴⁹ respectively. The large differences in theoretical EAs was attributed in Ref. ⁴⁸ to correlation of the 5d shell, which was included in their CCSD calculations but neglected in the MR-CISD and MCDF work. Correlation of the 5d electrons was calculated in their work to contribute 1.84 kcal/mol to the EA, therefore accounting for the large difference between theory and experiment. In strong disagreement with previous work, Felfli et al. ⁵¹ calculated a much larger EA for Tl of 55.69 kcal/mol using the complex angular momentum (CAM) method, claiming the previously measured and calculated values for the EA of Tl corresponded to the binding energy of an excited Tl anion and not the ground state.

In the present work, the first ionization potentials and electron affinities of the heavy p-block elements Ga-Rn (without EAs for group 18) were calculated using a relativistic coupled-cluster-based Feller-Peterson-Dixon (FPD) composite approach that includes extrapolations to the complete basis set (CBS) limits with outer-core electron correlation at the scalar relativistic CCSD(T) level of theory, contributions of higher level electron correlation up to CCSDTQ, quantum electrodynamics (QED) contributions of the Lamb shift, and spin-orbit coupling with inclusion of the Gaunt interaction. Particular attention has been given to the accurate treatment of SO, investigating several four-component methods ranging from Dirac-Hartree-Fock to CCSD(T).

II. COMPUTATIONAL METHODS

The Feller-Peterson-Dixon (FPD) approach^{1,52,53} was used based on the coupled cluster singles and doubles (CCSD) with perturbative triples, CCSD(T), level of theory⁵⁴ with a sequence of correlation consistent basis sets including diffuse functions, aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP ($n = T, Q, 5$),⁵⁵⁻⁵⁹ in conjunction with relativistic small-core pseudopotentials (PPs). These PP-based sets were chosen over the analogous all-electron DKH sets⁶⁰ due to the availability of 5Z quality sets in the former, which can be expected to yield more

accurate CBS limits. Open-shell calculations employed restricted open-shell Hartree-Fock (ROHF) orbitals but the spin-restriction was relaxed in the solution of the CCSD equations, i.e., R/UCCSD(T).^{61,62} Additive contributions were then included for core-valence correlation effects from outer-core electrons, corrections for the pseudopotential approximation, higher levels of correlation beyond CCSD(T), lowest-order QED effects (Lamb shift), and spin-orbit coupling including the Gaunt interaction. The spin-orbit coupling calculations were carried out in the DIRAC16 package,⁶³ while all scalar relativistic CCSD(T) calculations were carried out using the MOLPRO suite of computational programs.⁶⁴ The higher order correlation calculations utilized the MRCC program⁶⁵ as interfaced with MOLPRO. The full FPD composite scheme used in this work was thus

$$E(FPD) = E_{CBS} + \Delta E_{CV} + \Delta E_{DK} + \Delta E_{HC} + \Delta E_{Lamb} + \Delta E_{SO} \quad (1)$$

The largest component to the composite energy is from the frozen-core CBS limit utilizing small-core relativistic pseudopotentials for inner core electrons (10 electrons for Ga-Kr, 28 electrons for In-Xe, and 60 electrons for Tl-Rn). Using the aug-cc-pwCV n Z-PP sets with $n=Q$ and 5, the SCF energies were extrapolated to the basis set limit using the two-point Karton-Martin scheme⁶⁶

$$E_n^{SCF} = E_{CBS}^{SCF} + A(n+1)e^{-9\sqrt{n}} \quad (2)$$

and the frozen-core (FC) (valence s and p electrons correlated) CCSD(T) correlation energies were extrapolated separately via⁶⁷

$$E_n^{corr} = E_{CBS}^{corr} + \frac{B}{(n+\frac{1}{2})^4} \quad (3)$$

It should be noted that using the aug-cc-pV n Z-PP basis sets for the latter step showed less than a 0.2 kcal/mol difference in the CBS limits for the IPs. Overall the difference between the explicitly calculated aug-cc-pwCV5Z IPs and the CBS limits varied from only about 0.1 kcal/mol to up to just under 1 kcal/mol.

Contributions for the correlation of outer-core electrons (ΔE_{CV}) were calculated using CCSD(T), also with the aug-cc-pwCV n Z-PP basis sets⁵⁹ with $n=Q$ and 5. These results were also extrapolated to the CBS limit using the same scheme as for the frozen core calculations. Since the same basis sets and CBS extrapolations were used for both the FC and core-valence (CV) calculations, there is no additivity error due to the separation of these correlation effects, and the

results are presented in this manner purely for assessing the importance of CV correlation. All electrons not included in the pseudopotential were correlated, which thus defines the outer-core as the 3s, 3p, 3d electrons for Ga-Kr; 4s, 4p, 4d electrons for In-Xe; and 5s, 5p, 5d electrons for Tl-Rn.

A correction for using the scalar relativistic PPs (ΔE_{DK}) was included by carrying out all-electron scalar relativistic calculations using the aug-cc-pwCVQZ-DK basis sets⁶⁸ for the 4p elements and the aug-cc-pwCVQZ-DK3 sets⁶⁰ for 5p and 6p elements. Correspondingly the second order Douglas-Kroll-Hess (DKH2) Hamiltonian was utilized for the 4p elements, while the third order DKH Hamiltonian (DKH3) was used for the 5p and 6p elements.^{3,4,69} Correlation of the outer-core electrons were included in these calculations, and the final pseudopotential correction is the difference between the corresponding all electron DKH and pseudopotential energies. It should be noted that the above choices of DKH2 and DKH3 yield nearly identical results as those from the eXact-2-Component (X2C) Hamiltonian.^{5,6} For instance in the IP of Th, use of X2C with an uncontracted aug-cc-pwCVTZ-DK3 basis set gave a PP correction that differed by only 0.02 kcal/mol from the DKH3 value.

Higher order electron correlation effects (ΔE_{HC}) beyond CCSD(T) were included using CCSD with full iterative triples (CCSDT)⁷⁰⁻⁷² and quadruples (CCSDTQ).⁷³⁻⁷⁵ The triples correction to the CCSD(T) results was calculated as the difference between CCSDT and CCSD(T) correlation energies using the aug-cc-pwCVTZ-PP basis sets, while a quadruples correction was defined as the energy difference between CCSDTQ and CCSDT, but using the aug-cc-pwCVDZ-PP sets. Both valence and outer-core electrons were correlated in these calculations.

A contribution due to lowest order QED effects (ΔE_{Lamb}), i.e., the vacuum polarization and self-energy comprising the Lamb shift, was calculated using a local model potential approach based on the work of Pyykkö and Zhao.⁷⁶ The full model potentials used are given in the supplementary material. The local potential was added to the 1-electron DKH2 or DKH3 Hamiltonians with the aug-cc-pwCVTZ-DK/-DK3 basis sets and all outer-core and valence electrons were correlated in CCSD(T) calculations. The resulting energies were compared to the DKH2 and DKH3 results without the local potential to yield this contribution.

All spin-orbit calculations were carried out using the DIRAC16 package with the default finite Gaussian nucleus model.⁶³ The total spin-orbit contribution includes the difference in

energy between a calculation using the 4-component (4-c) Dirac-Coulomb (DC) Hamiltonian using an approximate contribution to the (SS|SS) Coulomb integrals, see Ref. ⁷⁷, and that obtained with Dyal's spin-free Hamiltonian⁷⁸. The Gaunt interaction was also included by taking the difference between a 4-c Dirac-Coulomb-Gaunt (DCG) Dirac-Hartree-Fock (DHF) calculation and one with just the DC Hamiltonian. Tests were carried out on the IP of Pb explicitly including the (SS|SS) integrals, which yielded no change in the Gaunt contribution and a lowering of the SO contribution by just 0.05 kcal/mol. All open-shell DHF calculations were based on the average-of-configuration DHF (AoC-DHF) method. Individual DHF energies were obtained from complete open-shell configuration interaction (COS-CI) calculations.⁷⁹ The all-electron basis sets were always used completely uncontracted, either aug-cc-pVTZ-DK/-DK3 or aug-cc-pwCVQZ-DK/-DK3.^{60,68,80}

Up to four different methods were used to calculate the effects of SO within the 4-c DC Hamiltonian. These included the AoC-DHF method with a subsequent COSCI step, Kramers-restricted configuration interaction (KRCI),⁸¹⁻⁸³ Fock space CCSD (FS-CCSD),⁸⁴ and CCSD(T).⁸⁵ Both the KRCI and CCSD(T) calculations used AoC-DHF orbitals while FS-CCSD used closed-shell DHF orbitals from the required closed-shell reference states. The AoC-DHF and KRCI calculations utilized the aug-cc-pVTZ-DK/-DK3 basis sets, with the KRCI calculations including correlation of only the valence electrons with a virtual orbital cutoff of about 12 a.u. In the coupled cluster calculations, both valence-only correlation with aug-cc-pVTZ-DK/-DK3 basis sets, as well as valence plus outer-core d electrons correlated calculations in conjunction with the aug-cc-pwCVQZ-DK/-DK3 basis sets, were carried out. In these coupled cluster cases, both FS-CCSD and CCSD(T), the virtual orbital cut-off was always set to 600 a.u. The FS-CCSD calculations were carried out for the ionization potentials of the group 13 and 14 elements by attaching up to two electrons to the closed shell, group 12 reference states and for the group 17 and 18 elements by ionizing up to 2 electrons from the group 18 reference states. In regard to electron affinities, these could only be obtained at the FS-CCSD level of theory for the elements of groups 13, 16, and 17. Finally in the case of CCSD(T), inspection of the AoC-HF wavefunctions indicated that several of the atoms were very multideterminantal when spin-orbit coupling was included. Hence accurate spin-orbit corrections for IPs could only be calculated at this level of theory for the elements of groups 13, 17, and 18, with the addition of the IP for Pb. Reliable CCSD(T) EAs could be obtained for groups 16 and 17 with the addition of Tl. The IPs

of Bi and Po, as well as the EAs of Pb and Bi, were borderline cases, but are preferred in this work over the KRCI values. In the CCSD(T) cases, calculations including correlation of the outer-core p electrons, i.e., 3p for Ga-Kr, 4p for In-Xe, and 5p for Tl-Rn, were also carried out using uncontracted aug-cc-pwCVTZ basis sets. Upon comparing these results to analogous calculations that only correlated the valence+d electrons, this contribution was added to the CCSD(T)/aug-cc-pwCVQZ valence+d values to obtain the final CCSD(T) spin-orbit effects on the IPs and EAs.

III. RESULTS

A. Ionization Potentials

Table I shows the contributions of spin-orbit coupling, including the Gaunt contributions, to the ionization potentials of this work using various 4-c methods (AoC-DHF, KRCI, FS-CCSD, and CCSD(T)). Also included in Table I are the estimated SO effects obtained from *J*-averaging the experimental energy levels (where available), as well as the semi-experimental results from Ref. ¹² for the 4p elements (*J*-average of experiment for 1st-order SO and ab initio for 2nd-order). Not unexpectedly, the total contribution of SO on the IPs increases down a particular group and is very significant for the 6p elements, reaching over 30 kcal/mol for the IP of Bi. The impact of the Gaunt term is relatively small, never reaching more than a few tenths of a kcal/mol even for the 6p elements. The current Gaunt contributions for Bi, Po, and At (+0.02, -0.16, and -0.10 kcal/mol) are in good agreement with the full Breit values previously presented by Borschevsky et al.⁴⁷ (0.00, -0.02, and -0.02 kcal/mol). In the course of this work, GRASP2K calculations⁸⁶ were also undertaken to calculate the Breit contribution to the IP of Pb with a result that differed by only -0.03 kcal/mol from the current Gaunt value. In general the use of *J*-averaging is accurate to within a few tenths of a kcal/mol for both the 4p and 5p elements, with the worst differences appearing to occur for the cases of Te and I where differences of more than 1 kcal/mol is observed in comparison with 4c-DC-KRCI or CCSD(T). As shown in Table I, this approach significantly breaks down for the heavier 6p elements. For the 4p and 5p elements, electron correlation for the SO contribution is not particularly important, with the largest correlation effect calculated to be just 0.4 kcal/mol for iodine. Effects on the SO contribution due to electron correlation becomes much more important for the 6p elements, as much as 5 kcal/mol

for Po, and there is more sensitivity to which correlation method is utilized. In contrast to the lighter elements, 4c-CCSD(T) could be reliably used in SO calculations for the entire 6p period.

As shown in Table II, outside of SO effects, the largest contribution to the frozen-core CCSD(T)/CBS IPs is due to the correlation of outer-core electrons, ΔCV . This contribution, which ranges from about 1–4 kcal/mol and always increases the IPs of these elements, becomes larger down each group and slightly decreases across a given period. In the case of the Pb atom, the effects of correlating the 4f electrons using a fully uncontracted aug-cc-pwCVQZ basis set and CCSD(T) was found to increase the IP by less than 0.001 kcal/mol. As shown in Table II, the effect of the PP approximation is nearly negligible in all cases, with the largest difference as compared to an all-electron DKH3 treatment of just -0.34 kcal/mol for the IP of Tl. Likewise, electron correlation beyond CCSD(T), as judged by CCSDT and CCSDTQ calculations, is even less important for these atomic IPs; only two atoms had ΔHC contributions as large as 0.1 kcal/mol, Ge and Rn. Finally, contributions to the IP due to the Lamb shift were calculated to be small and positive, ranging from +0.05 kcal/mol for Ga to +0.17 kcal/mol for Pb. The present $\Delta Lamb$ values can be compared to the QED contributions reported by Borschevsky et al.⁴⁷ for Bi, Po, and At. For those elements the present calculations result in $\Delta Lamb$ contributions of about +0.17 kcal/mol, which are only slightly larger than their QED values of about +0.14 kcal/mol.

After including SO contributions, including Gaunt, the final composite IPs agree with experiment to within a mean unsigned error of just 0.19 kcal/mol (standard deviation of 0.24 kcal/mol). The only deviations from experiment above 0.14 kcal/mol for the 4p and 5p elements occur for As, Se, and Sb, which deviate from experiment by +0.31, -0.22, and +0.78 kcal/mol, respectively. Note that in each of these cases, frozen-core KRCI calculations had to be used for the SO contributions. For the 6p elements, the only errors with respect to experiment above 0.21 kcal/mol are found for Pb (-0.66 kcal/mol) and Po (+0.56 kcal/mol). Presumably this is also due to the SO treatment, even though 4c-DC-CCSD(T) could be used in these cases. It is not obviously due to additivity errors, however, as indicated by the CBS-extrapolated 4c-DC-CCSD(T) results shown in Table II, which are nearly identical to the PP-based FPD values. Last, our final composite results for I and At can be compared to the 4c-CCSD(T)+Breit results of Rothe et al.,³¹ 241.15 and 214.95 kcal/mol from this work compared to 240.44 and 214.63

kcal/mol from theirs. As shown in Table II, the experimental values are 241.01 and 214.87 kcal/mol for I and At, respectively.

B. Electron Affinities

Analogous to the results shown for the ionization potentials discussed above, the SO contributions to the atomic electron affinities are given in Table III with the FPD component breakdowns with comparisons to available experiment being shown in Table IV. The Gaunt and SO results of Table III exhibit very similar trends as those of Table I for the ionization potentials; the magnitude of the SO effect increases down a group and the Gaunt contribution is generally very small. Valence electron correlation effects on SO, as judged by the difference between AoC-DHF and KRCI results, are modest for the 4p and 5p elements where it is generally only a few tenths of a kcal/mol but is very important for the 6p atoms, particularly Tl, Pb, and Bi. As in the IPs, attempting to correlate the outer-core electrons with the KRCI method did not lead to accurate results since it tended to strongly overestimate core correlation effects, presumably due to size extensivity errors. Results using simple J -averaging of the experimental energy levels, which are only available for the 4p and 5p EAs, appears to be accurate to within a few tenths of a kcal/mol, except for the EA of Te where comparison to CCSD(T) indicates an error of about 1.4 kcal/mol.

In comparing the FS-CCSD results for SO effects to CCSD(T) in Table III, it is clear that there is a degradation in accuracy when the calculation involves either the (0,2) or (2,0) sectors, i.e., when the orbitals employed are obtained from reference atomic states differing by 2 electrons from the state of interest. This is clearly seen in the EA results for Tl (Tl⁻ differs by 2 electrons from the Tl⁺ reference state) and particularly the group 17 elements, e.g., Po (neutral Po differs by 2 electrons from the Po²⁻ reference state), where they differ from the CCSD(T) values (without (n-1)p correlation) from 0.8 to 2.3 kcal/mol. This can also be observed for the IPs of Table I, albeit to a lesser extent; the FS-CCSD SO contributions to the IPs of both Pb and At differ from their CCSD(T) values by -0.6 kcal/mol.

As shown in Table IV, the effects of outer-core electron correlation are much smaller than for the IPs with the ΔCV values for the EAs of all atoms calculated to be less than 1 kcal/mol. In addition, both the PP correction (ΔDK) and QED effects ($\Delta Lamb$) are calculated to be even smaller than in the IP cases and are never more than about 0.1 kcal/mol. The effects of electron

correlation beyond CCSD(T) are also relatively small, although they do reach a few tenths of a kcal/mol for the 3p atoms and the early 4p atoms. After including the SO effects from Table III, the final FPD EAs are generally in excellent agreement with the available experimental values, except for the group 13 atoms. Without the group 13 atoms, the FPD EAs differ from experiment by an unsigned average of just 0.23 kcal/mol with a standard deviation of only 0.24 kcal/mol. Maximum deviations occur for Sn (0.6 kcal/mol) and Bi (0.7 kcal/mol) and these can be attributed to the SO treatment. As in the IPs, additivity in the FPD scheme does not limit the final accuracy as judged by the close agreement of the 4c-DC-CCSD(T)/CBS[T,Q]+ Δ Gaunt+ Δ QED results with the current FPD values.

In the cases of the group 13 elements (Ga, In, Tl), the experimental values appear to be too large – by more than 4 kcal/mol for Ga and over 1 kcal/mol for both In and Tl. Particularly for Ga and In where the SO effects are not strongly influenced by electron correlation (see Table III), the expected uncertainty in the FPD values are conservatively estimated to be ± 0.5 kcal/mol. In the case of Tl where the 4c-CCSD(T) calculations of the SO effects appear to be very reliable based on the magnitudes of the T1 amplitudes and coefficients of the HF determinants in the AoC-DHF calculations, the uncertainty in the FPD result should also be better than ± 0.5 kcal/mol. In the case of Tl most previous calculations also were in similar disagreement with experiment, but the FS-CCSD calculations of Eliav et al.⁴⁸ attributed this to a lack of 5d electron correlation. Table V investigates this further at the 4c-DC-CCSD(T) level of theory with both the QZ basis sets of this work and the same basis set as Eliav et al., as well as extrapolations to the CBS limit, and with and without the inclusion of SO effects. In this work the contribution of 5d correlation to the EA of Tl is calculated to be only about +0.3 kcal/mol at the CBS limit, while Eliav et al. reported values from +1.8 to +2.3 kcal/mol. The present calculations, even those also at the FS-CCSD level of theory, do not support such a large 5d correlation contribution. Hence as in the cases of Ga and In, it is recommended that the experimental EAs of the group 13 elements be revisited by experiment. It should also be noted in passing that there were no indications that the ground state of Tl⁻ is not ³P₀, hence the very large EA for Tl calculated by Felfli et al.⁵¹ is not supported in this work.

As in the IPs, the current FPD values for the EAs of Bi, Po, and At can be compared to the recent 4c-DC-CCSD(T)+Breit+QED results of Borschevsky et al.⁴⁷ In each case the EAs differ by no more than 0.3 kcal/mol, which can be attributed to the different basis sets used and the lack

of higher electron correlation effects in their work. Quite recently Si and Froese Fischer⁸⁷ published extensive multiconfiguration DHF (MCDHF) calculations for the EAs of the group 17 atoms. Their results for Br and I differed from experiment by just 0.10 and 0.11 kcal/mol, respectively. By comparison, the FPD results of this work differed by 0.06 and 0.02 kcal/mol, respectively. In the case of the EA of At, however, the MCDHF results of Ref. ⁸⁷ yielded a value of 54.72 ± 0.11 kcal/mol, which differs from the present FPD result by 1.11 kcal/mol. It also similarly differs from the 4c-DC-CCSD(T)+Breit+QED value of Borschevsky et al.⁴⁷ The Si and Froese Fischer result is well outside the uncertainty estimate of the present work, which recommends an EA for At of 55.8 ± 0.3 kcal/mol after attempting to account for all possible sources of error. It is not clear what the origin of this discrepancy might be.

IV. CONCLUSIONS

The relativistic FPD composite approach has been used to accurately determine the first ionization potentials and electron affinities for the post-*d*, *p*-block elements Ga – Rn. After extrapolation to the CBS limit, including the effects of outer-core electron correlation at the CCSD(T) level of theory, higher order electron correlation, QED, and SO effects were included to yield the final FPD results. Several different methods were investigated for the calculation of the SO effects on the IPs and EAs, all using 4-component wavefunctions with the Dirac-Coulomb Hamiltonian. In the cases where 4c-DC-CCSD(T) could be used for the SO contributions, the final IPs and EAs agreed with the available experimental values with an unsigned average error of just 0.16 (12 out of 18 cases) and 0.20 (6 out of 10 cases) kcal/mol, respectively. Otherwise when KRCI was utilized the error increased by several tenths of a kcal/mol. In all cases, however, the final errors with respect to experiment were below 1 kcal/mol. The exceptions were the EAs for the group 13 elements (Ga, In, Tl) where the accepted experimental values appear to be too large in all three cases. The values predicted in this work, which have conservative uncertainties of ± 0.5 kcal/mol, are 5.25 (Ga), 7.69 (In), and 7.39 (Tl) kcal/mol. For the EAs of Po and At, the current calculations predict values of 34.21 and 55.83 kcal/mol with estimated uncertainties of ± 0.6 and ± 0.3 kcal/mol, respectively.

SUPPLEMENTARY MATERIAL

See the supplementary material for the functional form and parameters for the model potentials used in the QED calculations for each atom.

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REFERENCES

- ¹ K. A. Peterson, D. Feller, and D. A. Dixon, *Theor. Chem. Acc.* **131**, (2012).
- ² M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).
- ³ G. Jansen and B. A. Hess, *Phys. Rev. A* **39**, 6016 (1989).
- ⁴ M. Reiher and A. Wolf, *J. Chem. Phys.* **121**, 10945 (2004).
- ⁵ M. Iliaš and T. Saue, *J. Chem. Phys.* **126**, 064102 (2007).
- ⁶ W. Liu and D. Peng, *J. Chem. Phys.* **131**, 031104 (2009).
- ⁷ B. Finney, Z. Fang, J. S. Francisco, and D. A. Dixon, *J Phys Chem A* **120**, 1691 (2016).
- ⁸ B. Maiti, G. C. Schatz, and G. Lendvay, *J. Phys. Chem. A* **108**, 8772 (2004).
- ⁹ J. S. Cohen and B. Schneider, *J. Chem. Phys.* **61**, 3230 (1974).
- ¹⁰ J. Tatchen and C. M. Marian, *Chem. Phys. Lett.* **313**, 351 (1999).
- ¹¹ S. Hofener, R. Ahlrichs, S. Knecht, and L. Visscher, *ChemPhysChem* **13**, 3952 (2012).
- ¹² N. J. DeYonker and K. A. Peterson, *J Chem Phys* **138**, 164312 (2013).
- ¹³ C. S. Nash and B. E. Bursten, *Ang Chem Int Ed* **38**, 151 (1999).
- ¹⁴ C. S. Nash and B. E. Bursten, *J. Phys. Chem. A* **103**, 402 (1999).
- ¹⁵ J. H. M. Neijzen and A. Donszelmann, *Physica B & C* **114**, 241 (1982).
- ¹⁶ J. Sugar and A. Musgrove, *J. Phys. Chem. Ref. Data* **22**, 1213 (1993).
- ¹⁷ K. S. Bhatia and W. E. Jones, *Can. J. Phys.* **49**, (1971).
- ¹⁸ B. Lindgren and H. P. Palenius, *Solar Physics* (1977).
- ¹⁹ J. L. Tech, *J. Re. Natl. Bur. Stand. (U.S.)* **67A**, (1963).
- ²⁰ S. Yoon and W. L. Glab, *J. Phys. B* **27**, 4133 (1994).
- ²¹ C. M. Brown, S. G. Tilford, and M. L. Ginter, *J. Opt. Soc. Am.* **67**, (1977).
- ²² R. Beigang and J. J. Wynne, *J. Opt Soc America B* **3**, 949 (1986).
- ²³ C. E. Moore, *Atomic Energy Levels*. (NSRDS-NBS 35; Office of Standard Reference Data, National Bureau of Standards, Washington DC, 1971).
- ²⁴ L. Minnhagen, *Ark. Fys.* **21**, (1962).
- ²⁵ R. D. Knight and L. Wang, *J. Opt Soc America B* **2**, 1084 (1985).
- ²⁶ F. Brandi, I. Velchev, W. Hogervorst, and W. Ubachs, *Phys. Rev. A* **64**, (2001).
- ²⁷ M. A. Baig and J. P. Connerade, *J. Phys. B* **18**, 1101 (1985).
- ²⁸ D. Wood and K. L. Andrew, *J. Opt. Soc. Am.* **58**, (1968).
- ²⁹ C. W. Matthews, M. L. Ginter, D. S. Ginter, and C. M. Brown, *J. Opt. Soc. Am. B* **6**, (1989).

- ³⁰ G. W. Charles, J. Opt. Soc. Am. **56**, (1966).
- ³¹ S. Rothe, A. N. Andreyev, S. Antalic, A. Borschevsky, L. Capponi, T. E. Cocolios, H. De Witte, E. Eliav, D. V. Fedorov, V. N. Fedosseev, D. A. Fink, S. Fritzsche, L. Ghys, M. Huyse, N. Imai, U. Kaldor, Y. Kudryavtsev, U. Koster, J. F. Lane, J. Lassen, V. Liberati, K. M. Lynch, B. A. Marsh, K. Nishio, D. Pauwels, V. Pershina, L. Popescu, T. J. Procter, D. Radulov, S. Raeder, M. M. Rajabali, E. Rapisarda, R. E. Rossel, K. Sandhu, M. D. Seliverstov, A. M. Sjodin, P. Van den Bergh, P. Van Duppen, M. Venhart, Y. Wakabayashi, and K. D. Wendt, Nat Commun **4**, 1835 (2013).
- ³² E. Rasmussen, Z. Phys. **80**, (1933).
- ³³ W. W. Williams, D. L. Carpenter, A. M. Covington, M. C. Koepnick, D. Calabrese, and J. S. Thompson, J. Phys. B: At. Mol. Opt. Phys. **31**, L341 (1998).
- ³⁴ D. Breteau, P. Babilotte, C. Drag, and C. Blondel, J. Phys. B **48**, 125001 (2015).
- ³⁵ C. W. Walter, N. D. Gibson, R. L. Field, A. P. Snedden, J. Z. Shapiro, C. M. Janczak, and D. Hanstorp, Phys. Rev. A **80**, (2009).
- ³⁶ M. Vandevraye, C. Drag, and C. Blondel, Phys. Rev. A **85**, (2012).
- ³⁷ C. Blondel, P. Cacciani, C. Delsart, and R. Trainham, Phys. Rev. A **40**, 3698 (1989).
- ³⁸ C. W. Walter, N. D. Gibson, D. J. Carman, Y. G. Li, and D. J. Matyas, Phys. Rev. A **82**, (2010).
- ³⁹ M. Vandevraye, C. Drag, and C. Blondel, J. Phys. B **46**, 125002 (2013).
- ⁴⁰ M. Scheer, H. K. Haugen, and D. R. Beck, Phys. Rev. Lett. **79**, 4104 (1997).
- ⁴¹ G. Haeffler, A. E. Klinkmuller, J. Rangell, U. Berzinsh, and D. Hanstorp, Z. Phys. D **38**, 211 (1996).
- ⁴² R. J. Peláez, C. Blondel, C. Delsart, and C. Drag, J. Phys. B **42**, 125001 (2009).
- ⁴³ D. L. Carpenter, A. M. Covington, and J. S. Thompson, Phys. Rev. A **61**, 042501 (2000).
- ⁴⁴ X. Chen and C. Ning, J Chem Phys **145**, 084303 (2016).
- ⁴⁵ R. C. Bilodeau and H. K. Haugen, Phys. Rev. A **64**, (2001).
- ⁴⁶ R. J. Zollweg, J. Chem. Phys. **50**, 4251 (1969).
- ⁴⁷ A. Borschevsky, L. F. Pašteka, V. Pershina, E. Eliav, and U. Kaldor, Phys. Rev. A **91**, (2015).
- ⁴⁸ E. Eliav, Y. Ishikawa, P. Pyykko, and U. Kaldor, Phys. Rev. A **56**, 4532 (1997).
- ⁴⁹ W. P. Wijesundera, Phys. Rev. A **55**, 1785 (1997).

- ⁵⁰ F. Arnau, F. Mota, and J. J. Novoa, Chem. Phys. **166**, 77 (1992).
- ⁵¹ Z. Felfli, A. Z. Msezane, and D. Sokolovski, J. Phys. B **45**, 045201 (2012).
- ⁵² D. Feller, K. A. Peterson, and D. A. Dixon, J. Chem. Phys. **129**, (2008).
- ⁵³ D. Feller, K. A. Peterson, and D. A. Dixon, Mol. Phys. **110**, 2381 (2012).
- ⁵⁴ K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
- ⁵⁵ K. A. Peterson, J. Chem. Phys. **119**, 11099 (2003).
- ⁵⁶ K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, J. Chem. Phys. **119**, 11113 (2003).
- ⁵⁷ B. Metz, M. Schweizer, H. Stoll, M. Dolg, and W. Liu, Theor. Chem. Acc. **104**, 22 (2000).
- ⁵⁸ B. Metz, H. Stoll, and M. Dolg, J. Chem. Phys. **113**, 2563 (2000).
- ⁵⁹ K. A. Peterson and K. E. Yousaf, J Chem Phys **133**, 174116 (2010).
- ⁶⁰ D. H. Bross and K. A. Peterson, Theor. Chem. Acc. **133**, (2013).
- ⁶¹ J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
- ⁶² P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).
- ⁶³ DIRAC, a relativistic ab initio electronic structure program, Release DIRAC16 (2016), written by H. J. Aa. Jensen, R. Bast, T. Saue, and L. Visscher, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekstroem, E. Eliav, T. Enevoldsen, E. Fasshauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. Henriksson, M. Ilias, Ch. R. Jacob, S. Knecht, S. Komorovsky, O. Kullie, J. K. Laerdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. Di Remigio, K. Ruud, P. Salek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see <http://www.diracprogram.org>).
- ⁶⁴ MOLPRO, version 2015.1, a package of ab initio programs, 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, 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, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, , see <http://www.molpro.net>.

- ⁶⁵ MRCC, a string-based quantum chemical program suite written by M. Kállay. See also M. Kállay, P. R. Surján, *J. Chem. Phys.* **115** 2945 (2001) as well as: <http://www.mrcc.hu>. (2001).
- ⁶⁶ A. Karton and J. M. L. Martin, *Theor. Chem. Acc.* **115**, 330 (2006).
- ⁶⁷ J. M. L. Martin, *Chem. Phys. Lett.* **259**, 669 (1996).
- ⁶⁸ N. J. DeYonker, K. A. Peterson, and A. K. Wilson, *J. Phys. Chem. A* **111**, 11383 (2007).
- ⁶⁹ B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986).
- ⁷⁰ J. Noga and R. J. Bartlett, *J. Chem. Phys.* **86**, 7041 (1987).
- ⁷¹ G. E. Scuseria and H. F. Schaefer, *Chem. Phys. Lett.* **152**, 382 (1988).
- ⁷² J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **93**, 6104 (1990).
- ⁷³ M. Kállay and P. R. Surján, *J. Chem. Phys.* **115**, 2945 (2001).
- ⁷⁴ S. A. Kucharski and R. J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991).
- ⁷⁵ S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **97**, 4282 (1992).
- ⁷⁶ P. Pyykkö and L.-B. Zhao, *J. Phys. B* **36**, 1469 (2003).
- ⁷⁷ L. Visscher, *Theor. Chem. Acc.* **98**, 68 (1997).
- ⁷⁸ K. G. Dyall, *J. Chem. Phys.* **100**, 2118 (1994).
- ⁷⁹ O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort, *J. Chem. Phys.* **96**, 2910 (1992).
- ⁸⁰ A. K. Wilson, K. A. Peterson, D. E. Woon, and T. H. Dunning, Jr., *J. Chem. Phys.* **110**, 7667 (1999).
- ⁸¹ T. Fleig, J. Olsen, and L. Visscher, *J. Chem. Phys.* **119**, 2963 (2003).
- ⁸² T. Fleig, H. J. A. Jensen, J. Olsen, and L. Visscher, *J. Chem. Phys.* **124**, (2006).
- ⁸³ J. Olsen, P. Jorgensen, and J. Simons, *Chem. Phys. Lett.* **169**, 463 (1990).
- ⁸⁴ L. Visscher, E. Eliav, and U. Kaldor, *J. Chem. Phys.* **115**, 9720 (2001).
- ⁸⁵ L. Visscher, T. J. Lee, and K. G. Dyall, *J. Chem. Phys.* **105**, 8769 (1996).
- ⁸⁶ P. Jönsson, G. Gaigalas, J. Bieroń, C. F. Fischer, and I. P. Grant, *Comp. Phys. Commun.* **184**, 2197 (2013).
- ⁸⁷ R. Si and C. Froese Fischer, *Phys. Rev. A* **98**, 052504 (2018).
- ⁸⁸ Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2018). NIST Atomic Spectra Database (ver. 5.6.1), [Online]. Available: <https://physics.nist.gov/asd> [2018, November 19]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: <https://doi.org/10.18434/T4W30F>.

⁸⁹ H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).

Table I. Calculated Gaunt and spin-orbit contributions to the ionization potentials (kcal/mol).

			Gaunt	SO (Dirac-Coulomb)			
	J Avg. ^a	Ref. ¹²	AoC-DHF ^b	AoC-DHF ^b	KRCI ^c	FS-CCSD ^d	CCSD(T) ^{e,f}
Ga	+1.57	+1.59	-0.09	+1.51	+1.44	+1.55	+1.60
Ge	-0.60	-0.46	-0.08	-0.50	-0.44	-0.48	g
As	-5.05	-5.09	+0.00	-5.07	-4.90	h	g
Se	+2.70	+2.58	-0.15	+2.64	+2.51	h	g
Br	-0.70	-1.32	-0.09	-1.21	-1.27	-1.36	-1.25
Kr	-5.12	-5.01	-0.06	-5.10	-4.95	-4.97	-5.05
In	+4.22		-0.17	+4.17	+3.90	+4.19	+4.33
Sn	-1.05		-0.14	-0.32	-0.01	-0.11	g
Sb	-11.90		+0.01	-11.97	-11.59	h	g
Te	+6.02		-0.20	+5.43	+4.89	h	g
I	-1.56		-0.10	-3.78	-3.98	-4.49	-4.26
Xe	-10.04		-0.09	-9.73	-9.36	-9.36	-9.54
Tl	+14.85		-0.39	+15.93	+14.90	+15.50	+16.15
Pb	-2.47		-0.36	+5.81	+7.26	+6.91	+7.71
Bi	-39.75		+0.02	-36.26	-33.82	h	-34.17
Po	+18.43		-0.16	+6.31	+2.50	h	+1.41 ⁱ
At	---		-0.10	-16.41	-16.78	-18.07	-17.65
Rn	---		-0.11	-25.73	-24.61	-24.74	-24.87

^a Using the experimental energy levels⁸⁸ (where available) within the ground state terms.

^b Using uncontracted aug-cc-pVTZ basis sets

^c Valence electrons correlated with uncontracted aug-cc-pVTZ basis sets.

^d Valence plus outer-core d electrons correlated with uncontracted aug-cc-pwCVQZ basis sets.

^e CBS-extrapolated results with valence plus outer-core d electrons correlated using aug-cc-pwCVnZ (n=T, Q) basis sets with Eqs. (4) and (5), but Eq (4) used an exponent of 6.57 for the DHF component.

^f Contains CCSD(T)/aug-cc-pwCVTZ(unc) contributions from (n-1)p electron correlation of +0.02 (Ga), +0.02 (Br), -0.02 (Kr), +0.08 (In), -0.07 (I), -0.06 (Xe), +0.31 (Tl), +0.20 (Pb), -0.20 (Bi), -0.24 (Po), -0.20 (At), and -0.14 (Rn) kcal/mol. See the text.

^g Too multideterminantal for CCSD(T) with spin-orbit included. See the text.

^h Not applicable for FS-CCSD (more than 2-electrons from closed shell reference state).

ⁱ Borderline cases for reliable CCSD(T) calculations.

Table II: Contributions to composite FPD Ionization Potentials (kcal/mol).

	CBS	+ Δ CV	+ Δ DK	+ Δ HC	+ Δ Lamb	Pre- Δ SO Total	+ Δ SO ^a	Final FPD	4c-DC- CCSD(T) ^b	Expt. ^c
Ga	134.88	+1.81	+0.02	+0.08	+0.05	136.83	+1.51	138.34	138.60	138.35 ¹⁵
Ge	180.74	+1.77	+0.03	+0.10	+0.05	182.68	-0.52	182.16		182.17 ¹⁶
As	229.13	+1.68	+0.02	+0.05	+0.06	230.94	-4.90	226.04		225.73(1) ¹⁷
Se	220.83	+1.27	+0.10	+0.05	+0.06	222.32	+2.36	224.68		224.90 ¹⁸
Br	272.32	+1.22	+0.20	+0.01	+0.06	273.81	-1.34	272.47	272.81	272.43 ¹⁹
Kr	326.72	+1.13	+0.00	-0.05	+0.07	327.86	-5.11	322.75	323.22	322.84 ²⁰
In	126.81	+2.24	+0.05	+0.07	+0.09	129.26	+4.16	133.42	133.30	133.44 ¹⁵
Sn	166.85	+2.38	-0.01	+0.07	+0.09	169.37	-0.15	169.22		169.35 ²¹
Sb	208.44	+2.37	-0.05	+0.02	+0.09	210.87	-11.58	199.29		198.51 ²²
Te	200.92	+1.93	-0.01	+0.02	+0.09	202.95	+4.69	207.64		207.77 ²³
I	243.33	+1.95	+0.15	-0.02	+0.09	245.51	-4.36	241.15	241.25	241.01 ²⁴
Xe	287.44	+1.81	+0.11	-0.08	+0.09	289.37	-9.63	279.74	279.93	279.72 ^{25,26}
Tl	121.29	+3.75	-0.34	+0.03	+0.16	124.89	+15.76	140.65	140.55	140.86 ²⁷
Pb	159.03	+3.61	+0.20	+0.01	+0.17	163.02	+7.35	170.37	170.26	171.03 ²⁸
Bi	198.50	+3.39	+0.15	-0.03	+0.17	202.17	-34.15	168.02	168.02	168.01 ²⁹
Po	190.28	+2.75	+0.16	-0.02	+0.17	193.34	+1.25	194.59	194.38	194.03(9) ³⁰
At	229.91	+2.65	+0.03	-0.06	+0.16	232.70	-17.75	214.95	215.30	214.87 ³¹

Rn	270.43	+2.46	-0.04	-0.12	+0.16	272.90	-24.98	247.92	247.92	247.87 ³²
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^a Spin-Orbit contributions correspond to the sum of the Gaunt and CCSD(T) values of Table 2, except for Ge-Se and Sn-Te, where the Gaunt + KRCI results were utilized.

^b 4c-DC-CCSD(T)/aug-cc-pwCVTZ and /aug-cc-pwCVQZ results (valence+d correlated) extrapolated to the CBS limit via Eqs (4) and (5) with the addition of the Gaunt, QED, and (n-1)p SO correlation effects. An exponent of 6.57 was used in Eq. (4) instead of 9, which is appropriate for a TZ/QZ extrapolation.

^c Uncertainties less than 0.01 kcal/mol unless otherwise noted.

Table III. Calculated spin-orbit contributions to the electron affinities (kcal/mol).

		Gaunt	SO (Dirac-Coulomb)			
	J Avg. ^a	AoC-DHF ^b	AoC-DHF ^b	KRCI ^c	FS-CCSD ^d	CCSD(T) ^{e,f}
Ga	-0.44	+0.01	-0.55	-0.50	-0.56	g
Ge	-2.77	+0.05	-2.75	-2.63	h	g
As	+1.39	-0.03	+1.45	+1.36	h	g
Se	-0.53	+0.01	-0.75	-0.77	-1.50	-0.82
Br	-3.51	+0.03	-3.45	-3.35	-3.42	-3.43
In	-1.11	+0.01	-1.34	-0.95	-1.12	g
Sn	-7.06	+0.07	-7.01	-6.73	h	g
Sb	+3.45	-0.06	+3.37	+3.02	h	g
Te	-1.25	+0.01	-2.32	-2.46	-4.03	-2.65
I	-7.25	+0.02	-6.85	-6.57	-6.84	-6.75
Tl	---	+0.01	-4.86	-1.12	-1.35	-0.48
Pb	---	+0.17	-23.73	-21.85	h	-22.22 ⁱ
Bi	---	-0.02	+6.85	+3.70	h	+3.08 ⁱ
Po	---	+0.05	-10.03	-10.54	-13.52	-11.35
At	---	+0.05	-17.81	-17.10	-17.28	-17.39

^a Using the experimental energy levels⁸⁹ (where available) within the ground state terms.

^b Using uncontracted aug-cc-pVTZ basis sets

^c Valence electrons correlated with uncontracted aug-cc-pVTZ basis sets.

^d Valence plus outer-core d electrons correlated with uncontracted aug-cc-pwCVQZ basis sets.

^e CBS-extrapolated results with valence plus outer-core d electrons correlated using aug-cc-pwCVnZ (n=T, Q) basis sets with Eqs. (4) and (5), but Eq (4) used an exponent of 6.57 for the DHF component.

^f Contains CCSD(T)/aug-cc-pwCVTZ(unc) contributions from (n-1)p electron correlation of -0.02 (Se), -0.02 (Br), -0.05 (Te), -0.05 (I), +0.03 (Tl), -0.20 (Pb), -0.09 (Bi), -0.13 (Po), -0.10 (At) kcal/mol. See the text.

^g Too multideterminantal for CCSD(T) with spin-orbit included. See the text.

^h Not applicable for FS-CCSD (more than 2-electrons from closed shell reference state).

ⁱ Borderline cases for reliable CCSD(T) calculations.

Table IV. Contributions to composite FPD Electron Affinities (kcal/mol).

	CBS	+ Δ CV	+ Δ DK	+ Δ HC	+ Δ Lamb	Pre- Δ SO Total	+ Δ SO ^a	Final FPD	4c-DC- CCSD(T) ^b	Expt. ^c
Ga	7.64	-0.43	-0.01	+0.24	+0.02	7.46	-2.21	5.25		9.45(92) ^d
Ge	31.03	-0.01	+0.01	+0.17	+0.03	31.23	-2.58	28.65		28.43 ³⁴
As	16.93	-0.16	+0.01	+0.25	+0.03	17.07	+1.33	18.40		18.54 ³⁵
Se	47.08	+0.08	+0.06	+0.12	+0.04	47.38	-0.81	46.57	46.66	46.60 ³⁶
Br	80.59	+0.21	+0.08	-0.02	+0.04	80.91	-3.40	77.51	77.76	77.57 ³⁷
In	9.98	-0.41	+0.01	+0.21	+0.05	9.85	-2.16	7.69		9.32(21) ³⁸
Sn	32.49	+0.16	+0.10	+0.12	+0.06	32.93	-6.67	26.26		25.64 ³⁹
Sb	20.84	-0.04	+0.06	+0.19	+0.05	21.10	+2.96	24.06		24.15 ⁴⁰
Te	47.77	+0.29	+0.03	+0.08	+0.06	48.22	-2.64	45.58	45.66	45.45 ⁴¹
I	76.68	+0.49	+0.10	-0.05	+0.06	77.29	-6.73	70.56	70.75	70.54 ⁴²
Tl	7.36	+0.34	-0.06	+0.13	+0.08	7.86	-0.47	7.39	7.27	8.69(30) ⁴³
Pb	29.46	+0.88	+0.05	+0.06	+0.11	30.56	-22.05	8.51	8.47	8.23 ⁴⁴
Bi	18.58	+0.51	+0.05	+0.13	+0.09	19.38	+3.06	22.44	22.28	21.73 ⁴⁵
Po	44.51	+0.81	+0.07	+0.02	+0.10	45.51	-11.30	34.21	34.22	---
At	72.15	+0.95	+0.06	-0.09	+0.11	73.17	-17.34	55.83	55.88	---

^a Spin-Orbit contributions correspond to the sum of the Gaunt and CCSD(T) values of Table 4, except for Ga-As and In-Sb, where the Gaunt + KRCI results were utilized.

^b 4c-DC-CCSD(T)/aug-cc-pwCVTZ and /aug-cc-pwCVQZ results (valence+d correlated) extrapolated to the CBS limit via Eqs (4) and (5) with the addition of the Gaunt, QED, and (n-1)p SO correlation effects. An exponent of 6.57 was used in Eq. (4) instead of 9, which is appropriate for a TZ/QZ extrapolation.

^c Uncertainties less than 0.01 kcal/mol unless otherwise noted.

^d Value of Ref. ³³ corrected for the anion fine structure. See Ref. ⁸⁹

Table V. Contributions to the electron affinity of Tl from correlating the outer-core electrons (kcal/mol).

Method	Electrons correlated	ΔEA^a
DK3-CCSD(T)/aug-cc-pwCVTZ-DK3 ^b	val+5s5p5d	+0.08
DK3-CCSD(T)/aug-cc-pwCVQZ-DK3 ^b	val+5s5p5d	+0.29
DK3-CCSD(T)/CBS ^b	val+5s5p5d	+0.34
PP-CCSD(T)/aug-cc-pwCVQZ-PP ^b	val+5s5p5d	+0.24
PP-CCSD(T)/aug-cc-pwCV5Z-PP ^b	val+5s5p5d	+0.30
DK3-CCSD(T)/aug-cc-pwCVQZ-DK3 ^b	val+5d	+0.28
X2C-CCSD(T)/Eliav ^c	val+5d	+0.36
DC-FS-CCSD/Eliav ^c	val+5d	+0.23
Eliav (Scheme 12) ^d	val+5d	+1.84
Eliav (Scheme 11) ^d	val+5d	+2.31

^a Change in the EA relative to just correlating the 6s6p valence electrons.

^b This work. The TZ, QZ, and 5Z sets include maximum angular momenta of g, h, and i, respectively, optimized for 5d5p5d correlation.

^c From this work using the same basis set as Ref. ⁴⁸, which has maximum angular momentum of i-type.

^d FS-CCSD results of Ref. ⁴⁸.