

Systematically convergent basis sets with relativistic pseudopotentials. I. Correlation consistent basis sets for the post-*d* group 13–15 elements

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Systematically convergent basis sets with relativistic pseudopotentials.

I. Correlation consistent basis sets for the post-*d* group 13–15 elements

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New correlation consistent-like basis sets have been developed for the post-*d* group 13–15 elements (Ga–As, In–Sb, Tl–Bi) employing accurate, small-core relativistic pseudopotentials. The resulting basis sets, which are denoted cc-pVnZ-PP, are appropriate for valence electron correlation and range in size from (8s7p7d)/[4s3p2d] for the cc-pVDZ-PP to (16s13p12d3f2g1h)/[7s7p5d3f2g1h] for the cc-pV5Z-PP sets. Benchmark calculations on selected diatomic molecules (As₂, Sb₂, Bi₂, AsN, SbN, BiN, GeO, SnO, PbO, GaCl, InCl, TlCl, GaH, InH, and TIH) are reported using these new basis sets at the coupled cluster level of theory. Much like their all-electron counterparts, the cc-pVnZ-PP basis sets yield systematic convergence of total energies and spectroscopic constants. In several cases all-electron benchmark calculations were also carried out for comparison. The results from the pseudopotential and all-electron calculations were nearly identical when scalar relativity was accurately included in the all-electron work. Diffuse-augmented basis sets, aug-cc-pVnZ-PP, have also been developed and have been used in calculations of the atomic electron affinities. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622923]

I. INTRODUCTION

In nearly all *ab initio* electronic structure calculations two basis set expansions dictate the overall accuracy attainable, the *N*-electron wave function is expanded in products of 1-electron orbitals and in turn these orbitals are generally described by linear combinations of Gaussian-type functions. This latter basis set, which is the topic of the present work, is in practice always incomplete and this limits the accuracy with which the Schrödinger equation can be solved with a given choice of wave function method. The interplay between the errors that are intrinsic to a given wave function method and those associated with the underlying Gaussian basis set can greatly confuse any subsequent assessment of the overall accuracy of the calculation. Following the work of Jankowski *et al.*,¹ the introduction of atomic natural orbital (ANO) basis sets by Almlöf and Taylor² and the development of correlation consistent basis sets by Dunning³ allowed for the first time the systematic extension of the 1-particle basis set towards the complete basis set (CBS) limit in correlated calculations. For a given correlation consistent basis set, a shell of correlating functions are included whereby each function in the shell contributes similar amounts of correlation energy in correlated atomic calculations. As a series of these basis sets are used, the total correlation energy converges nearly exponentially towards the CBS limit. The family of correlation consistent basis sets (cc-pVnZ) has now been extended by Dunning and co-workers to include elements as heavy as krypton.^{4,5} Augmentations of the standard cc-pVnZ basis sets to describe anions, hydrogen bonding, van der Waals interactions, and core-valence correlation effects have also been reported.^{6,7} Over

the last several years techniques have been developed that involve the extrapolation to the approximate complete basis set (CBS) limit using the results from calculations with increasing sizes of (aug-)cc-p(C)VnZ basis sets (cf., Ref. 8, and references therein). In particular, this has had a very large impact on the resulting accuracy of thermochemical and spectroscopic predictions by *ab initio* methods.

By their construction, standard correlation consistent basis sets are all-electron sets, i.e., all electrons of an atom are explicitly described by basis functions. In many respects this is advantageous since no additional approximations are made, but this approach can also lead to very large basis sets for heavier elements in order to adequately describe the low-lying core electrons. In addition, both scalar and spin-orbit relativistic effects must then also be treated using all-electron methods, which can often lead to relatively high computational costs for accurate results. On the other hand, a nearly effortless way to accurately recover relativistic effects involves the use of relativistic effective core potentials (ECPs) or pseudopotentials (PPs). The accuracy of the PP approximation naturally depends on the method of adjustment, but in particular it can be critically dependent on the number of electrons included in the core. With large-core PP's only a minimal number of valence electrons are retained, while small-core PP's retain both the valence and semi-core electrons. For example, for the As atom a large-core PP would include 28 electrons in the core ([Ar]+3d) while a small-core PP might include just 10. For valence atomic orbitals of angular symmetry with counterparts in the core, the resulting valence pseudo-orbitals have a greatly reduced number of radial nodes. For large-core PPs they are nodeless, and it has been shown⁹ that this leads to an overestimation of valence electron correlation energies compared to all-electron work

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by as much as 10%. This can largely be mitigated by the use of small-core PPs, which results in at least one radial node in these same valence pseudo-orbitals. Other problems with large-core PPs in molecular calculations include additional errors due to core penetration effects, as well as inadequate Pauli repulsion between valence electrons on one center with the PP core on another.¹⁰ Recently Stoll, Dolg, and co-workers have reported a new set of small-core relativistic PPs adjusted in multiconfiguration-Dirac-Hartree-Fock (MCDHF) calculations.^{11,12} At the time this work began, these were only available for the post- d group 13–15 elements, which is the subject of this work. Pseudopotentials of this variety have now been adjusted for the post- d group 16–18 elements; these new PPs and basis sets analogous to the ones described here are the subject of the following paper in this issue.¹³

While an appropriate choice of PP can yield accurate scalar and spin-orbit relativistic effects, the accompanying basis sets can also be much smaller compared to all-electron sets due to the absence of the low-lying core electrons. While most PPs in the literature provide their own basis sets, these are generally of only double- or triple-zeta quality and do not allow for a systematic expansion towards the CBS limit like the family of all-electron correlation consistent basis sets. Recently there have been a couple of studies involving correlation consistent-like basis sets developed in conjunction with relativistic PPs. Bauschlicher¹⁴ has developed sequences of basis sets for use with both large- and small-core PPs for the In atom and reported their use in thermochemical studies of indium chlorides.¹⁵ More recently Martin and Sundermann¹⁶ reported a series of correlation consistent-like basis sets for Ga–Kr and In–Xe that utilized large-core Stuttgart–Dresden–Bonn PPs (with some small-core studies included for Ga, Ge, and In). Their SDB-cc-pVnZ ($n = T, Q$) basis sets were then used in several small molecule benchmark calculations. Schwerdtfeger and co-workers¹⁷ have reported a series of cc-like basis sets for Hg. Like in the works of both Bauschlicher¹⁴ and Martin and Sundermann,¹⁶ their basis sets utilized a single HF set, but in their case all exponents were optimized at the MP2 level of theory. In addition, the present author has recently reported¹⁸ the development of correlation consistent-like basis sets for both Y and Hg that are similar in form to those described in this work.¹⁸ Lastly, Osanai *et al.*¹⁹ have recently reported ANO-type basis sets in conjunction with relativistic model core potentials for all of the same atoms of the present work, while Dolg and co-workers²⁰ have reported the development of ANO basis sets with PPs for various lanthanides and actinide elements.

In this study, correlation consistent basis sets have been developed for the post- d group 13–15 elements (Ga–As, In–Sb, Tl–Bi) in conjunction with the small-core MCDHF-adjusted PPs of Stoll, Dolg, and co-workers, which retain the nsp and $(n-1)spd$ electrons. Series of basis sets from double- through quintuple-zeta are described and are denoted by cc-pVnZ-PP (correlation consistent polarized valence n - ζ with pseudopotentials). These sets are developed to systematically converge both the Hartree-Fock and valence electron correlation energies to their CBS limits. The methodol-

ogy used is described in Sec. II, while the actual basis set development is described in Sec. III. Molecular benchmark calculations on selected closed-shell diatomics using these new sets are also described in Sec. III. Lastly, the results are summarized in Sec. IV.

II. METHODOLOGY

All of the exponent (ζ) optimizations in this work were carried out using a BFGS algorithm²¹ using double-sided numerical derivatives. The actual optimizations were performed in a scaled parameter space and the gradients were generally converged to better than 1×10^{-6} a.u. The MOLPRO program suite²² was employed for all calculations and only the pure spherical harmonic components of the $dfg\dots$ angular momentum functions were used. Full symmetry equivalent of the orbitals was used in all cases, however this was not enforced at the correlated levels of theory. Unless otherwise noted, only the valence electrons ($4s4p$ for Ga–As, $5s5p$ for In–Sb, $6s6p$ for Tl–Bi) were correlated, and in all cases the newly reported, small-core PPs of Metz *et al.* were utilized.^{11,12} These PPs were optimized at the MCDHF level of theory and have been shown to provide an accurate description of both scalar and spin-orbit relativistic effects. The core definitions corresponded to [Ne], [Ar]+ $3d$, and [Kr]+ $4d4f$ for the post- $3d$, $-4d$, and $-5d$ elements, respectively (10, 28, and 60 electrons). In other words the $(n-1)spd$ and nsp electrons are always explicitly treated in the *ab initio* calculations.

The Hartree-Fock spd base sets that were used in the preliminary optimizations were taken from exponent expansions defined by $\zeta_k = \alpha\beta^{f(k)}$, where

$$f(k) = k \left[1 + \gamma \frac{k}{n} + \delta \left(\frac{k}{n} \right)^2 \right] \quad (1)$$

for $k=0,1,\dots,n-1$ ($k=0$ corresponds to the most diffuse exponent and n is the length of the expansion). These *extended even tempered* (ExtET) expansions were derived by modification of the usual $\zeta_k = \alpha\beta^k$ even tempered formula.²³ The ExtET form is similar to the usual well tempered expansion formula (cf., Ref. 24) and requires the optimization of four parameters ($\alpha, \beta, \gamma, \delta$). In the ExtET sets, however, the s , p , and d primitives are not constrained to belong to a common set of exponents as in the well tempered scheme. In particular, the functional form of Eq. (1) is based on a cubic polynomial fit to the spacings between $\ln(\zeta_k)$ within a given basis set of fully optimized exponents. By way of contrast, the usual even tempered formula is a linear approximation to this spacing. Particularly for fully-optimized, all-electron basis sets, the separation between exponents is generally a slowly increasing function of n , and the exponents are well fit by the ExtET form with the parameters γ and δ having typical values on the order of -1 for γ and $+1$ for δ . A related expansion in terms of Legendre functions has recently been reported by Petersson and co-workers.²⁵

The optimization of basis functions in the presence of an ECP does introduce some new issues that are not present in all-electron work. First, since the PP attempts to force the pseudo-orbital to zero in its inner regions, unconstrained exponent optimizations at the HF level can lead to near linear

dependency in the basis sets, i.e., the ratio of two neighboring exponents can be as small as 1.3 or less. This can be commonly observed in existing ECP basis sets in the literature. In the present work, the exponent optimizations were constrained so that the ratio of any two exponents in the same angular symmetry must be ≥ 1.6 . This choice, while fairly arbitrary, was found to yield a negligible effect on the energy while significantly decreasing linear dependencies. In addition, as recently shown by both Blaudeau *et al.*²⁶ and Christiansen,²⁷ single uncontracted correlating functions in ECP-based calculations are much less effective in recovering correlation energy than in all-electron calculations due to the interplay of the amplitudes and derivatives of these functions near the origin and the magnitude of the pseudo-orbitals in this region. The most straightforward solution to this problem was shown by Christiansen²⁷ to involve just including an extra correlating function in each symmetry. This prescription is investigated in detail in the next section.

For the most part, the correlating functions in this work were obtained using the singles and doubles configuration interaction (CISD) method. The values of the resulting exponents, however, were relatively insensitive to this choice as determined by tests at the coupled cluster, CCSD(T),²⁸ and averaged coupled pair functional²⁹ (ACPF) levels of theory. The exception to this in the present work was in the optimization of diffuse functions by calculations on the atomic anions. In these cases it was found that CCSD(T) provided the most systematic sequence of augmenting functions from aug-cc-pVDZ-PP through aug-cc-pV5Z-PP.

III. RESULTS AND DISCUSSION

The development of standard correlation consistent basis sets can generally be divided into four distinct steps:

- (1) Optimization of a series of correlation functions for the atom using a large Hartree–Fock (HF) base set—this establishes the identity and quantity of angular momentum functions that will be included in each correlation consistent basis set to systematically converge the correlation energy to its basis set limit;
- (2) Optimization of a series of *spd* HF sets that systematically converge to the HF limit;
- (3) Determination of how to best include correlating functions for angular momenta that correspond to occupied atomic orbitals, i.e., uncontract or add additional functions;
- (4) Optimization of augmenting functions for the description of electron affinities and weak interactions.

Each of these have been carefully examined in the present work with particular care being given to how the presence of a PP may affect the results in contrast to the experience with all-electron basis sets. In each of the following subsections, As, Sb, and Bi are taken to be representative elements of their respective rows. Analogous investigations were also made for Ga, In, and Tl but the trends were very similar and hence these results will not be explicitly shown.

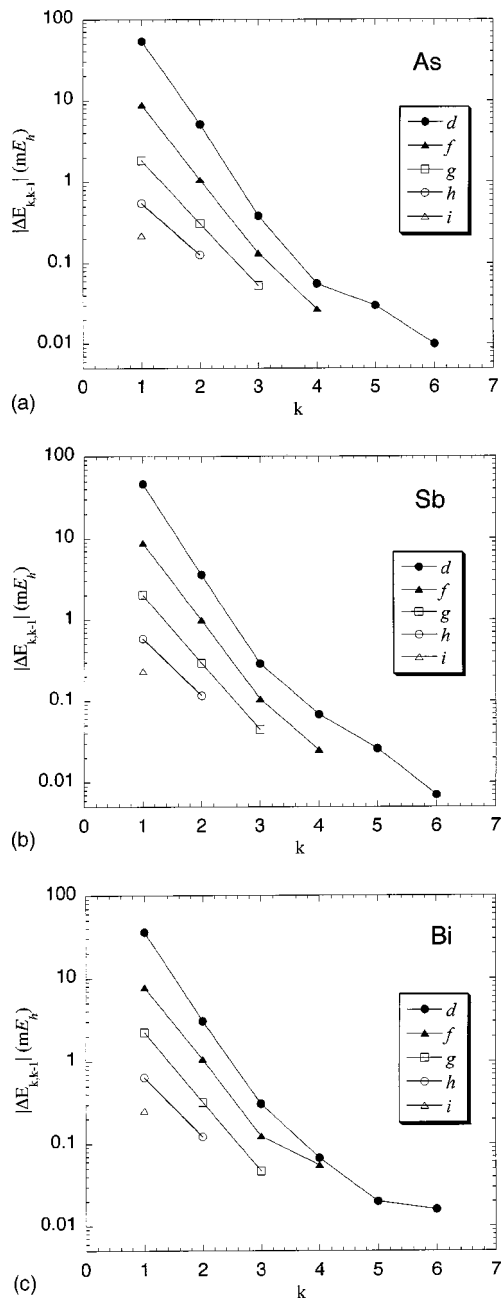


FIG. 1. Contributions of polarization functions to the CISD correlation energy of the ns^2np^3 electrons in (a) arsenic, (b) antimony, and (c) bismuth. The absolute values of the incremental correlation energy lowerings, $|\Delta E_{\text{corr}}|$, are plotted in mE_h against the number of functions in the expansions for *d**f**g**h**i* functions.

A. Establishing correlation consistency

In order to determine the correlation consistent groupings of *dfg*... correlating functions, CISD optimizations were carried out with a (14s13p11d) ExtET base set contracted to [6s6p1d] for As, Sb, and Bi. Even tempered expansions were used for the correlating functions. Figure 1 shows the incremental correlation energy recovered by the addition of correlating functions in valence-only CISD calculations on As, Sb, and Bi (5 electrons correlated in each case). After including up to 6 even tempered *d*-type functions, *f* functions were added to a [6s6p1d]+(4*d*) set, *g* functions were subsequently added to a [6s6p1d]

+ $(4d3f)$ set, h functions were added to a $[6s6p1d]$ + $(4d3f2g)$ set, and finally an i function was added to the $[6s6p1d] + (4d3f2g2h)$ set. The expected correlation consistent groupings are clearly apparent from Fig. 1, namely $(1d)$ for DZ, $(2d1f)$ for TZ, $(3d2f1g)$ for QZ, and $(4d3f2g1h)$ for 5Z. It should be noted that the plots of the incremental correlation energy are nearly identical for each element, and the one for arsenic is very similar to the all-electron results shown previously for the Se atom.⁵

As has also been noted in the development of all-electron main group cc-pVnZ basis sets for the second and third rows (Al–Ar and Ga–Kr, respectively),^{4,5} Fig. 1 shows that the addition of the first function of a given angular momentum is always slightly more energetically important than the addition of a second function of a lower angular momentum, e.g., the first f -type function recovers nearly twice as much correlation energy as the second d -type function. While as previously noted⁵ this could suggest a different prescription for including correlation functions within a given cc basis set, we will choose in this work to continue to retain the familiar groupings of the correlation consistent basis sets. As shown in detail below, this choice results in basis sets with the desired systematic convergence characteristics for both atoms and molecules.

In Fig. 1 a slight “knee” in the d series for As and Sb, as well as in the f series for Bi, can also be observed. In the all-electron cc-pVnZ basis sets for the second row atoms this change in convergence rate for the d functions at $n_d=4$ was later attributed to the need for additional high exponent d functions in the basis set.³⁰ While this may be the case for As at $n_d=5$ (corresponding to a 6Z basis set—this behavior also occurs with the all-electron work of Ref. 5), this does not appear to be the case for Sb since the most diffuse d exponents in this series continue to decrease and do not show the introduction of a high exponent function at the knee as in the second row atoms. For Bi, however, the decrease in the convergence rate at $n_f=4$ does appear to be due to an increased importance of high exponent f functions in the basis. However the energetic contribution is relatively small at this level and in any event $n_f=4$ would correspond to a 6Z basis set, which is also outside the scope of this work. The convergence rate of the f -type correlating functions for Bi was also investigated at the all-electron level using the Douglas–Kroll–Hess (DK) Hamiltonian³¹ for scalar relativity. With a cc-pV5Z-DK (spd only) base set (see below), the CISD-optimized f exponents were found to be nearly identical in value to the ones obtained in the PP calculations and the incremental correlation energy changes were also essentially identical. Hence the “knee” in the f convergence rate is not due to the use of the pseudopotential or, in particular, the lack of an explicitly occupied $4f$ shell in those calculations.

As mentioned above, it has been shown previously that when using PPs, single uncontracted primitive functions now make poor correlating functions. The initial results by Blaudeau *et al.*,²⁶ and particularly Christiansen,²⁷ indicated that s -type functions were most strongly affected, however the problem may also exist for p , d , and higher angular momentum functions as well. This has been investigated in detail in the present work by examining the incremental corre-

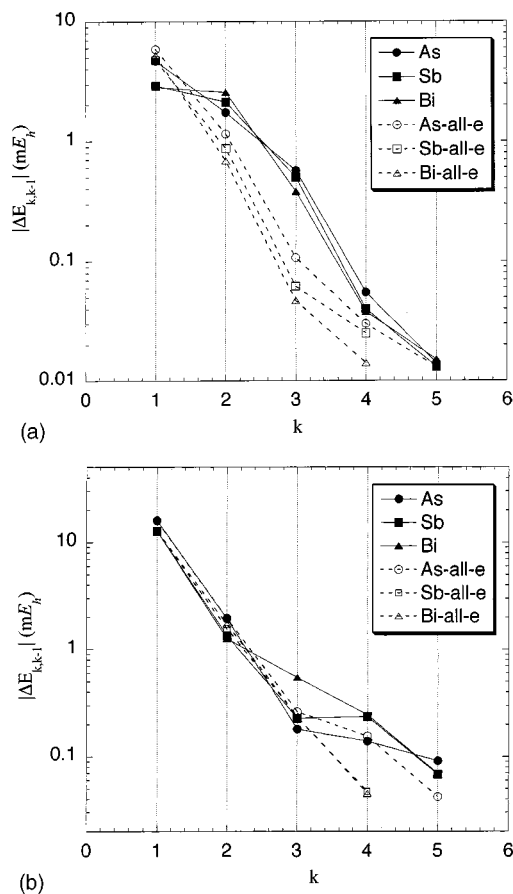


FIG. 2. The absolute values of the incremental CISD correlation energy lowerings in mE_h for (a) s -type and (b) p -type correlating functions in As, Sb, and Bi.

lation energy recovery of these functions at the CISD level of theory in atomic calculations. Figure 2 shows the incremental correlation energy recovered by s and p functions with base sets taken from the work of the above section of $[2s6p1d] + (4d3f2g)$ and $[6s2p1d] + (4d3f2g)$, respectively, for As, Sb, and Bi. In each case the results from all-electron DK calculations (using a cc-pV5Z-DK base set, see below) are also shown for comparison.

Focusing first on the contributions to the correlation energy due to the s functions, it is clearly observed that for the PP case the first s function for As does recover slightly less correlation energy than in the all-electron work. In addition, the optimized value for this exponent is relatively diffuse when compared to the all-electron result, i.e., 0.094 versus 0.127. Figure 2(a) also shows that the contributions from the second, third, etc. s functions fall off less rapidly in the PP case compared to the all-electron results. For the heavier Sb and Bi atoms, the first and second s correlating functions recover nearly the same amounts of correlation energy, and the all-electron DK results exhibit nearly twice the $1s$ correlation energy compared to the PP values and drop off much more rapidly, similar to As (the Sb and Bi first s correlating exponents were also much more diffuse than their all-electron counterparts). All of these points are strong confirmation of the work of Blaudeau *et al.*²⁶ and Christiansen²⁷ that single s -type primitives make poor correlating functions due to the presence of the PP.

In contrast to the series of s -type correlating functions, both the p -type [Fig. 2(b)] and d -type (Fig. 1) series exhibit smooth decreases in incremental correlation energy lowering between the first and second functions and all-electron optimizations yielded nearly identical results. For all three atoms it should be noted from Fig. 2 that the third and fourth p -type functions contribute similar amounts of incremental correlation energy when the PP is used; this appears to be due to the somewhat increased importance of large exponent p functions. For As this behavior is similar to that observed in the all-electron optimizations and is only slightly accentuated in the PP results. For both Sb and Bi the much slower convergence at $n_p=3$ is not present in all-electron optimizations for these elements.

On the basis of these results, the groupings of s and p correlating functions in the new cc-pVnZ-PP sets should be changed from the typical all-electron patterns to $(2s1p)$, $(3s2p)$, $(4s3p)$, and $(5s4p)$ for DZ-5Z, respectively, for the third row atoms and $(2s1p)$, $(3s2p)$, $(4s4p)$, and $(5s5p)$ for DZ-5Z, respectively, for the fourth and fifth row atoms.

B. Optimization of Hartree–Fock spd sets

One of the characteristics of standard, all-electron correlation consistent basis sets is that in addition to employing functions that systematically converge the correlation energy, they also utilize HF sets of increasing size that rapidly converge the HF energy. In a practical sense, this typically means that a cc-pVDZ basis set has a HF set that provides only a double- ζ description of the valence atomic orbitals, whereas the cc-pV5Z set is much closer to the HF-limit. Hence the construction of the most compact correlation consistent-type basis sets requires the optimization of a series of primitive HF sets for each atom. In the present work, spd HF primitive sets were optimized for each angular momentum separately using a $(14s13p11d)$ ExtET base set. Using As, Sb, and Bi as guides for the other elements, s sets from $(7s)$ – $(16s)$, p sets from $(6p)$ – $(13p)$, and d sets from $(5d)$ – $(13d)$ were fully optimized at the HF level.

At this point it should be mentioned that even though fewer primitive functions are required in the present case compared to all-electron work, which in itself greatly simplifies the optimizations, the exponent optimizations were often quite time consuming due to the existence of multiple minima. This seemed to mainly occur for angular symmetries that already possessed one radial node in the highest energy valence orbital, i.e., s and p . Additional small amplitude nodal structure would then typically occur at short range due to the PP forcing the pseudo-orbital to zero. Often exponents would get “trapped” between these nodes and the resulting solution was very dependent on the initial set of exponents. This trapping seemed to be much more pronounced than in all-electron optimizations. While significant effort was expended to obtain the lowest energy for a particular size of spd primitive set, it is always possible that a particular solution slightly lower in energy might exist. It should also be stressed that the present HF basis sets are only optimal for the specific choice of PPs used in this work.

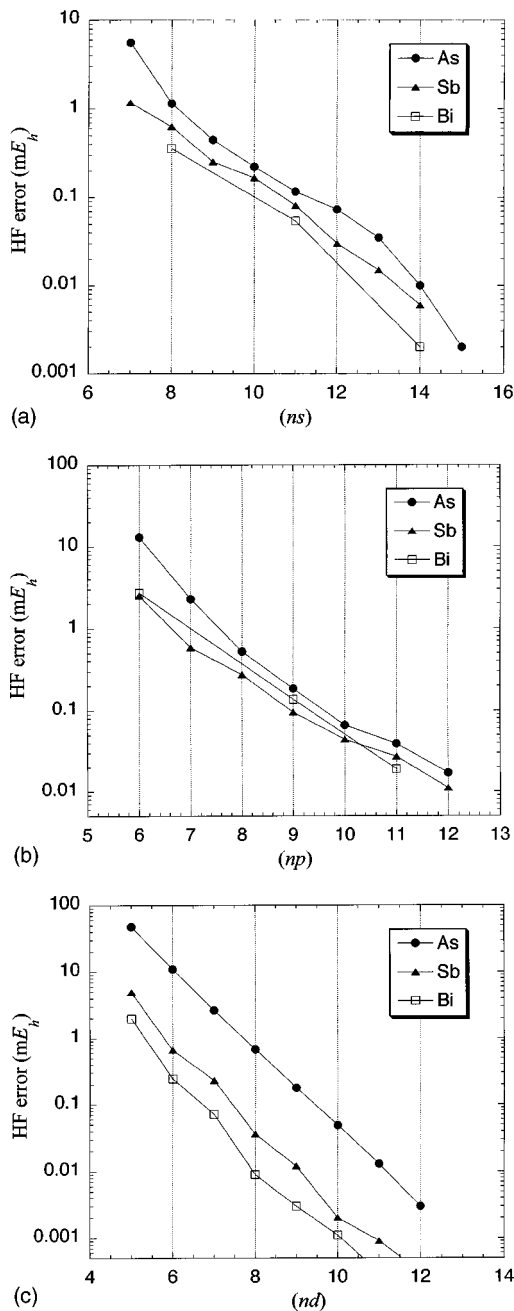


FIG. 3. Errors in the HF energy (in mE_h) relative to a $(16s13p13d)$ primitive set for various HF (a) s , (b) p , and (c) d sets in the As, Sb, and Bi atoms.

Figure 3 depicts the resulting HF errors for the series of optimized ns , np , and nd primitives for As, Sb, and Bi. In each case the errors are calculated relative to an optimized $(16s13p13d)$ set and not to an extrapolated limit. The rates of convergence towards the HF limit are observed to be fairly rapid and nearly exponential, although there is a little more variability in the ns series for As. In addition, while the rate of convergence is nearly the same for all three atoms, the relative errors for As are always larger than either Sb or Bi. This is particularly true for the nd series, where the relative errors for As are generally larger by an order of magnitude. In any event, it is clearly apparent from Fig. 3 that even with the use of small-core PPs, only relatively small expansions are required to closely approach the apparent HF limit.

C. Construction of cc-pVnZ-PP basis sets

With a series of HF primitive sets optimized, what remains is to determine which of these to match with a particular set of correlating functions to construct the final cc-pVnZ-PP basis sets. For the standard, all-electron cc-pVnZ sets this was determined primarily by two factors, the error in the HF energy should be smaller than that of the correlation energy and the most diffuse *spd* HF primitives should be suitable to replace some or all of the optimal correlating functions. In the present work the highest priority was placed on a rapid convergence towards the HF limit. In addition, like the cc-pVnZ basis sets, the DZ sets should have only 2 exponents describing the outermost region of the *s* and *p* valence orbitals, the TZ sets should have 3, and the outermost exponents should systematically decrease from one set to another. Based on all of these criteria, the following HF primitive sets were chosen:

cc-pVDZ-PP:

Ga–As: (8s7p6d)

In–Sb: (8s6p5d)

Tl–Bi: (8s6p5d)

cc-pVTZ-PP:

Ga–As: (10s9p8d)

In–Sb: (11s9p8d)

Tl–Bi: (11s9p7d)

cc-pVQZ-PP:

Ga–As: (14s11p11d)

In–Sb: (14s11p11d)

Tl–Bi: (14s11p10d)

cc-pV5Z-PP:

Ga–As: (16s13p12d)

In–Sb: (16s13p12d)

Tl–Bi: (16s13p11d).

It should be noted that a (6d) set is chosen for the cc-pVDZ-PP basis for the third row atoms in order to decrease the HF error. This is in contrast to their all-electron counterparts where (5d) sets were used. In addition, the (*nd*) sets for Tl–Bi (TZ-5Z) are generally smaller by 1 function compared to the other two rows due to the faster convergence of the HF energy in these cases.

The possibility of replacing some of the optimal (even tempered) *spd* correlating functions by uncontracting existing HF primitives was then investigated. In the case of the *s*-type correlating functions, it was found that in nearly all cases the required functions could be obtained by just uncontracting the most diffuse *s* exponents of the HF sets without incurring a significant increase in the correlation energy compared to the fully optimized cases. On the other hand, in the TZ basis sets for the fourth and fifth row elements, the

most diffuse HF *s* exponent was nearly identical to the most diffuse QZ *s* exponent and was significantly more diffuse than the smallest exponent in the optimal (3*s*) correlating set. Hence in these cases, only the second and third most diffuse *s* exponents were uncontracted from the HF set and an additional *s*-type correlating function was added that was equal to the geometric mean of the most diffuse *s* exponents in the DZ and QZ basis sets.

In the case of the *p*-type correlating functions, in most cases these were also just uncontracted from the HF sets. However, again at the TZ level, but now for all elements, the most diffuse *p* exponents (first and second or first and third) in the HF sets did not match up well at all with the optimal (2*p*) CISD correlating functions. Hence the CISD optimal functions were simply added in these cases. Lastly, in the case of the *d*-type correlating functions, the prescription followed in the all-electron post-3*d* cc-pVnZ basis sets⁵ involved adding the most diffuse optimal correlating *d* function to the basis and obtain any remaining functions by uncontracting from the HF set. This procedure resulted in very little raising of the correlation energy due to these substitutions. As expected, in the present case this also worked well for the post-3*d* elements, Ga–As. However for the post-4*d* and -5*d* elements, none of the HF *d* exponents were very optimal for use as correlating functions. In these cases, the most diffuse CISD optimal *d* function was still added to the basis as with the third row sets, but then the original (*nd*) primitive set was reoptimized at the HF level in the presence of this extra, fixed exponent. The resulting relaxation of the exponents then somewhat fortuitously yielded a new set of HF *d*'s in which the most diffuse members were found to be much more suitable for use as correlating functions.

The final compositions of the cc-pVnZ-PP basis sets were then:

cc-pVDZ-PP:

Ga–As (8s7p7d)/[4s3p2d]

In–Sb (8s6p6d)/[4s3p2d]

Tl–Bi (8s6p6d)/[4s3p2d],

cc-pVTZ-PP:

Ga–As (10s11p9d1f)/[5s4p3d1f]

In–Sb (12s11p9d1f)/[5s4p3d1f]

Tl–Bi (12s11p8d1f)/[5s4p3d1f],

cc-pVQZ-PP:

Ga–As (14s11p12d2f1g)/[6s5p4d2f1g]

In–Sb (14s11p12d2f1g)/[6s6p4d2f1g]

Tl–Bi (14s11p11d2f1g)/[6s6p4d2f1g],

cc-pV5Z-PP:

Ga–As (16s13p13d3f2g1h)/[7s6p5d3f2g1h]

In–Sb (16s13p13d3f2g1h)/[7s7p5d3f2g1h]

Tl–Bi (16s13p12d3f2g1h)/[7s7p5d3f2g1h].

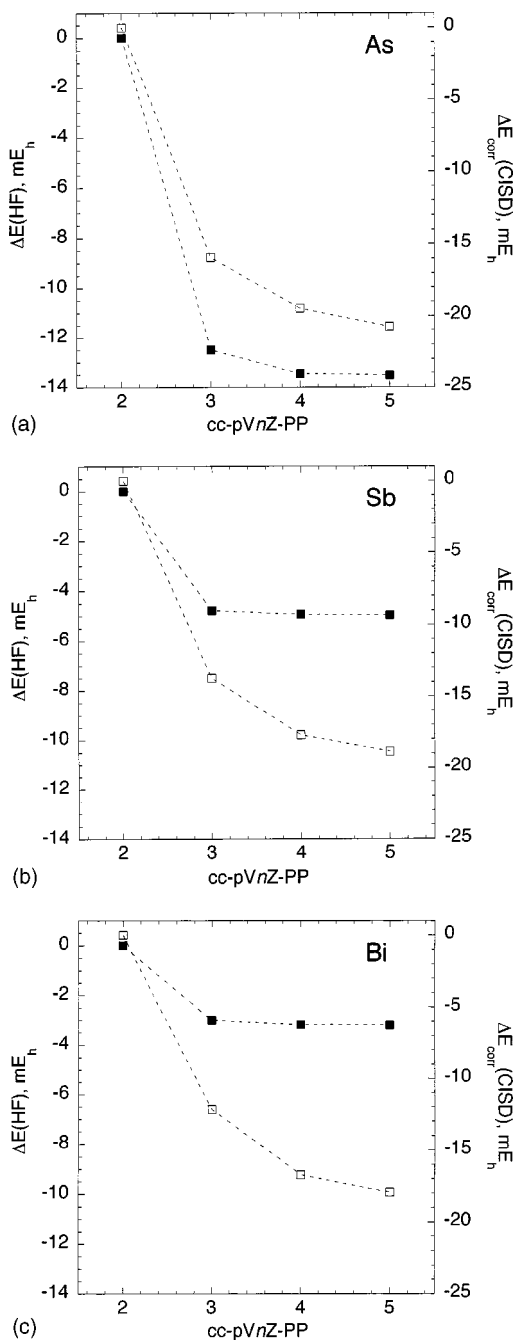


FIG. 4. Convergence of the HF energy (filled squares, left axes) and CISD correlation energy (open squares, right axes) as a function of the new cc-pVnZ-PP basis sets used for the (a) As, (b) Sb, and (c) Bi atoms.

The HF and CISD correlation energy convergence is plotted in Fig. 4 as a function of n in the cc-pVnZ-PP basis sets. The HF convergence is observed to be very rapid with near-HF limit results obtained even with the cc-pVQZ-PP basis sets. The slowest HF convergence occurs for the third row elements and can be mainly attributed to difficulties in describing the $3d$ orbitals. In all cases the convergence of the correlation energy appears to be very systematic and indicative of correlation consistent-like behavior. As shown below in molecular benchmark calculations, the well-behaved HF and correlation energy convergence is reflected in the systematic convergence of molecular energetics and spectroscopic constants.

D. All-electron cc-pV5Z-DK basis sets for As, Sb, and Bi

While the use of relativistic pseudopotentials provides a very convenient way to recover relativistic effects, as well as decreasing the overall computational expense, the effect of the pseudopotential approximation on the accuracy of the results is always a concern. Thus, it is important in the context of the present work to perform a few all-electron benchmark calculations with basis sets of very similar quality that accurately include scalar relativistic effects, e.g., using the DK Hamiltonian.³¹ All-electron cc-pVnZ basis sets are, of course, available for the post- $3d$ elements Ga–As, and their spd primitive sets can be easily recontracted in atomic DK calculations³² (subsequently denoted cc-pVnZ-DK). For the fourth and fifth row elements, suitably accurate basis sets were not available, hence basis sets of approximately 5Z quality have been developed in this work for both the Sb and Bi atoms. The Hartree–Fock primitive sets were optimized at the HF-DK level of theory using the ExtET formulation of Eq. (1), and even tempered sets of correlating functions were optimized at the CISD-DK level of theory. For the Sb atom, a (28s23p17d) HF primitive set was optimized. This size was chosen based on the well tempered nonrelativistic basis sets of Huzinaga and Klobukowski²⁴ and resulted in a valence triple zeta exponent distribution. For the Bi atom the analogous well-tempered set²⁴ corresponded to (28s24p18d12f), but at the HF-DK level of theory it was found necessary to increase this to (32s26p19d12f) within the ExtET scheme in order to obtain a valence triple zeta exponent distribution. For both Sb and Bi cc-pV5Z-DK basis sets were then constructed by first uncontracting the 4 most diffuse s and p primitives and the 3 most diffuse d primitives. A set of (1d3f2g1h) correlating functions optimized at the CISD-DK level of theory was then added in each case. The final cc-pV5Z-DK HF and CISD total energies were calculated to be -6476.508785 and $-6476.585809 E_h$, respectively, for Sb and -21510.190087 and $-21510.256364 E_h$, respectively, for Bi. It should be noted that for As, Sb, and Bi the valence CISD/cc-pV5Z-PP correlation energies were only slightly higher (+0.5, +0.7, and +0.4 mE_h , respectively, or 0.5%, 0.9%, and 0.6%) than the all-electron CISD/cc-pV5Z-DK values. As discussed in detail by Dolg,⁹ these small differences presumably arise from the altered nodal structure of the pseudo-orbitals, however these differences are much smaller than observed previously in large-core PP work.⁹

E. Atomic electron affinities: aug-cc-pVnZ-PP basis sets

For the description of atomic and molecular anions, as well as hydrogen bonding and van der Waals interactions, it is well known that additional diffuse functions must be added to most standard basis sets. In the spirit of the standard correlation consistent basis sets, aug-cc-pVnZ-PP basis sets have been constructed from the cc-pVnZ-PP sets by adding shells of diffuse functions that consisted of single, uncontracted basis functions in each angular symmetry appearing in these sets. As in the all-electron aug-cc-pVnZ basis sets,

TABLE I. CCSD(T) total energies and electron affinities for the post-*d* group 13–15 atoms. The total energies ($E_{\text{CCSD(T)}}$) are in hartrees and the electron affinities (EA) are in kcal/mol. Only the valence *ns* and *np* electrons have been correlated.

Atom	Basis set	$E_{\text{CCSD(T)}}$		EA ^a
		Anion	Neutral	
Ga	aug-cc-pVDZ-PP	-258.344 770	-258.334 999	6.13
	aug-cc-pVTZ-PP	-258.361 504	-258.349 970	7.24
	aug-cc-pVQZ-PP	-258.363 821	-258.351 903	7.48
	aug-cc-pV5Z-PP	-258.364 362	-258.352 304	7.57
	Experiment			6±3
Ge	aug-cc-pVDZ-PP	-293.444 891	-293.399 482	28.49
	aug-cc-pVTZ-PP	-293.467 937	-293.419 412	30.45
	aug-cc-pVQZ-PP	-293.471 463	-293.422 293	30.85
	aug-cc-pV5Z-PP	-293.472 478	-293.423 101	30.98
	Experiment			31.20±0.07
As	aug-cc-pVDZ-PP	-331.283 600	-331.270 346	8.32
	aug-cc-pVTZ-PP	-331.321 221	-331.298 522	14.24
	aug-cc-pVQZ-PP	-331.328 422	-331.303 005	15.95
	aug-cc-pV5Z-PP	-331.330 581	-331.304 382	16.44
	Experiment			16.0±0.7
In	aug-cc-pVDZ-PP	-189.257 922	-189.244 471	8.44
	aug-cc-pVTZ-PP	-189.267 696	-189.252 436	9.58
	aug-cc-pVQZ-PP	-189.269 263	-189.253 551	9.86
	aug-cc-pV5Z-PP	-189.269 729	-189.253 894	9.94
	Experiment			7±5
Sn	aug-cc-pVDZ-PP	-213.432 850	-213.385 190	29.91
	aug-cc-pVTZ-PP	-213.448 509	-213.397 610	31.94
	aug-cc-pVQZ-PP	-213.451 579	-213.399 961	32.39
	aug-cc-pV5Z-PP	-213.452 483	-213.400 656	32.52
	Experiment			32.70±0.09
Sb	aug-cc-pVDZ-PP	-239.352 699	-239.334 026	11.72
	aug-cc-pVTZ-PP	-239.381 261	-239.352 710	17.92
	aug-cc-pVQZ-PP	-239.388 406	-239.356 855	19.80
	aug-cc-pV5Z-PP	-239.390 390	-239.358 064	20.28
	Experiment			18.7±1.2
Tl	aug-cc-pVDZ-PP	-171.554 268	-171.544 460	6.15
	aug-cc-pVTZ-PP	-171.561 491	-171.550 332	7.00
	aug-cc-pVQZ-PP	-171.563 338	-171.551 683	7.31
	aug-cc-pV5Z-PP	-171.563 879	-171.552 111	7.38
	Experiment			5±5
Pb	aug-cc-pVDZ-PP	-191.916 233	-191.872 529	27.42
	aug-cc-pVTZ-PP	-191.928 670	-191.882 381	29.05
	aug-cc-pVQZ-PP	-191.932 020	-191.885 033	29.48
	aug-cc-pV5Z-PP	-191.933 025	-191.885 845	29.61
	Experiment			32.76±0.18
Bi	aug-cc-pVDZ-PP	-213.655 453	-213.639 329	10.12
	aug-cc-pVTZ-PP	-213.679 730	-213.654 745	15.68
	aug-cc-pVQZ-PP	-213.687 253	-213.659 347	17.51
	aug-cc-pV5Z-PP	-213.689 203	-213.660 540	17.99
	Experiment			3.4±0.2

^aExperimental values from Ref. 41 have been approximately corrected for spin-orbit effects by averaging the atomic multiplets. Where atomic data was not available (all but Ge, Sn, and Pb), the anion multiplet splittings were taken to be identical to the isoelectronic neutral atoms. Errors due to the latter approximation are not reflected in the quoted experimental uncertainties. Due to the large experimental uncertainties in the EA's of In and Tl, this correction was not applied in these cases.

these additional functions were optimized for the atomic anions; the *s* and *p* functions at the HF level of theory and the *d* and higher angular momentum functions with a correlated method. While initially these latter functions were optimized at the CISD level of theory, it was found in this work that slightly more reliable exponent distributions (as judged by their smooth variance with *n*) were obtained in CCSD(T) optimizations. Exponents obtained with the latter method

(most of which were nearly identical to their CISD counterparts) were used in the final aug-cc-pVnZ-PP basis sets.

The resulting atomic electron affinities calculated at the CCSD(T) level of theory are explicitly shown in Table I and are depicted in Fig. 5. Smooth convergence towards their basis set limiting values is observed in each case. Excellent agreement with experiment is also observed near the CBS limit when effects due to spin-orbit coupling are taken into

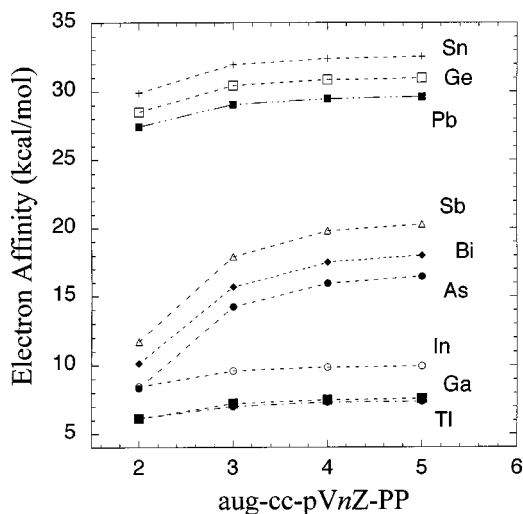


FIG. 5. Calculated CCSD(T) electron affinities (in kcal/mol) as a function of the aug-cc-pVnZ-PP basis sets.

account. This, of course, is reflective of the intrinsic accuracy of the CCSD(T) method. As shown in Table I, an exception is the electron affinity of the Bi atom, but this is presumably due to inaccuracies in estimating the experimental average of the atomic multiplet of the anion from the level spacings of Po. In particular, simple j -averaging within a single multiplet neglects important intraconfiguration SO interactions that will certainly be important for an element as heavy as Po/Bi⁻. In addition, spin-orbit effects on the Bi atom itself are non-negligible; recent SO calculations on Bi(⁴S) demonstrated an energy lowering of nearly 13 kcal/mol.³³ A systematic study of the spin-orbit effects in these species using the new basis sets is currently planned. Comparison of the current results for Ga, Ge, and As to the nonrelativistic all-electron CCSD(T)/aug-cc-pVnZ electron affinities reported by Wilson *et al.*,⁵ suggests that scalar relativity decreases the EA's by 0.6–0.9 kcal/mol. This has been confirmed in the present work by a relativistic all-electron CCSD(T)/aug-cc-pV5Z-DK calculation of the EA of As, 16.46 kcal/mol, which is within 0.02 kcal/mol of the CCSD(T)/aug-cc-pV5Z-PP value given in Table I and 0.84 kcal/mol smaller than the nonrelativistic value cited in Ref. 5. Similar all-electron aug-cc-pV5Z-DK calculations have also been carried out for the electron affinities of Sb and Bi. These results are within 0.03 and 0.12 kcal/mol, respectively, of the cc-pV5Z-PP values given in Table I.

F. Molecular benchmark calculations

In order to validate the new cc-pVnZ-PP basis sets in molecular calculations, benchmark studies were carried out on the near-equilibrium potential energy functions of a variety of closed-shell diatomics: homonuclear (As₂, Sb₂, Bi₂), nitrides (AsN, SbN, BiN), oxides (GeO, SnO, PbO), chlorides (GaCl, InCl, TlCl), and hydrides (GaH, InH, TlH) at the CCSD(T) level of theory. The potential energy functions were characterized by 9 points over the range $-0.4a_0 \leq r - r_e \leq +0.7a_0$ and were well fit by sixth to eighth order polynomials in simple internal displacement coordinates.

Spectroscopic constants were determined from a Dunham analysis³⁴ using the fitted polynomial coefficients. The dissociation energies were calculated relative to atomic asymptotes where full symmetry equivalencing was imposed on the orbitals and the R/UCCSD(T) method was used.³⁵ Before comparing the calculated dissociation energies to the experimental values, the latter were adjusted by the known spin-orbit splitting in the atoms³⁶ since the *ab initio* results of this work do not include spin-orbit coupling effects. Except for the case of the chlorides, the standard cc-pVnZ or cc-pVnZ-DK basis sets were used for all the non post- d elements, while the aug-cc-pVnZ or aug-cc-pVnZ-DK basis sets were used for Cl to describe its anionic character in GaCl, InCl, and TlCl.

Lastly, since the present basis sets are appropriate only for valence electron correlation, which does not include the $(n-1)d$ electrons of these elements, special consideration had to be given to all of the heteronuclear diatomics except the hydrides. Specifically, the N and O $2s$ orbitals, as well as the Cl $3s$ orbital, tended to strongly mix with the $(n-1)d_{\sigma}$ orbital of the heavy atoms since they have very similar orbital energies (in some cases their ordering with respect to energy would switch). In order to obtain reliable valence correlated results as defined here by the correlation of only the ns and np electrons, the $2s$ (N,O) or $3s$ (Cl) orbitals and the $(n-1)d_{\sigma}$ orbital were subjected to a Boys localization procedure at the HF level of theory, which unambiguously allowed leaving the d_{σ} orbitals in the core. A similar treatment for InCl was reported previously by Schwerdtfeger *et al.*³⁷ Spectroscopic constants calculated from potential energy functions where the orbital localization was not carried out exhibited much larger errors compared to experiment due to mixing valence and core-valence correlation effects in an unbalanced manner. However even after orbital localization, relatively large errors in the spectroscopic constants still exist even with the cc-pV5Z-PP basis sets, especially for the equilibrium bond lengths, but these residual errors can mainly be attributed to pure core-valence correlation effects. For example, previous calculations on GaCl and GeO have indicated bond length contractions of ~ 0.02 and ~ 0.01 Å, respectively,¹⁶ upon correlating the semicore electrons, while even larger core-valence correlation effects have been reported for TlCl.¹¹ Augmentation of the present basis sets to accurately describe core-valence correlation will be the subject of a separate investigation.

Tables II–VI contain the results of CCSD(T) calculations on homonuclear diatomics, nitrides, oxides, chlorides, and hydrides, respectively. In general, the convergence of the spectroscopic constants with respect to the cc-pVnZ-PP basis set used is very regular and reminiscent of results obtained in all-electron studies with cc-pVnZ sets. The convergence trends are well represented by the results for the homonuclear diatomics in Table II. The convergence with basis set of their calculated equilibrium bond lengths and dissociation energies are depicted in Fig. 6. Both quantities exhibit typical correlation consistent-like convergence towards their apparent CBS limits. Clearly the basis set extrapolation techniques that have been so successful in the last few years

TABLE II. CCSD(T) total energies and spectroscopic constants calculated for As₂, Sb₂, and Bi₂ compared to experiment.

Basis	E_{\min} (E_h)	E_{∞} (E_h)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	D_e (kcal/mol)
As ₂						
cc-pVDZ-PP	-662.642 639	-662.533 446	2.1448	414.03	1.10	68.52
cc-pVTZ-PP	-662.724 166	-662.595 653	2.1259	424.01	1.01	80.64
cc-pVQZ-PP	-662.742 656	-662.605 920	2.1194	427.59	0.99	85.80
cc-pV5Z-PP	-662.749 104	-662.609 019	2.1175	429.14	0.98	87.90
all-electron:						
cc-pVQZ	-4 468.800 625	-4 468.663 223	2.1284	428.73	0.99	86.22
cc-pV5Z	-4 468.807 628	-4 468.666 833	2.1263	430.21	0.99	88.35
cc-pVQZ-DK	-4 518.212 670	-4 518.076 333	2.1214	427.05	0.98	85.55
cc-pV5Z-DK	-4 518.220 253	-4 518.080 610	2.1194	428.48	0.98	87.63
Expt. ^a			2.1026	429.55	1.12	91.9
Sb ₂						
cc-pVDZ-PP	-478.737 678	-478.662 261	2.5554	256.83	0.61	47.32
cc-pVTZ-PP	-478.797 445	-478.704 152	2.5316	266.86	0.52	58.54
cc-pVQZ-PP	-478.815 190	-478.713 667	2.5211	270.19	0.51	63.71
cc-pV5Z-PP	-478.821 107	-478.716 395	2.5188	271.33	0.50	65.71
all-electron:						
cc-pV5Z-DK	-12 953.284 333	-12 953.180 300	2.5224	270.72	0.50	65.28
Expt. ^b			2.476	269.62	0.56	69.45
Bi ₂						
cc-pVDZ-PP	-427.334 722	-427.274 159	2.7227	172.58	0.40	38.00
cc-pVTZ-PP	-427.384 921	-427.307 917	2.6909	182.64	0.31	48.32
cc-pVQZ-PP	-427.402 948	-427.318 424	2.6793	184.76	0.29	53.04
cc-pV5Z-PP	-427.408 814	-427.321 176	2.6767	185.62	0.29	54.99
all-electron:						
cc-pV5Z-DK	-43 020.606 728	-43 020.519 132	2.6743	186.05	0.28	54.97
Expt. ^c			2.6596	173.06	0.38	47

^aReference 42.^bReference 43.^cReferences 44 and 42.

should also be of similar value with the new cc-pVnZ-PP basis sets.

Comparison of the cc-pV5Z-PP results of Table II with the all-electron cc-pV5Z-DK values reveals differences on average of just 0.0026 Å for r_e and 0.24 kcal/mol for D_e . Of course, while the basis sets are very similar between cc-pV5Z-PP and cc-pV5Z-DK, different treatments of scalar relativity are also used. In any event, it appears that the new basis sets together with the small-core PP's of Stoll, Dolg, and co-workers have an accuracy essentially identical to all-electron relativistic calculations in the absence of spin-orbit coupling. In the case of As₂, comparison of nonrelativistic calculations with the standard cc-pV5Z basis set with the relativistic cc-pV5Z-DK values show that inclusion of scalar relativity results in reductions of the equilibrium bond distance by 0.0069 Å and the dissociation energy by 0.72 kcal/mol. Comparison of the CCSD(T)/cc-pV5Z-PP results to experiment for the most part show errors of the expected size considering the neglect of core-valence correlation and residual basis set errors. An exception appears to be the equilibrium bond distance in Sb₂, where the experimental value appears to be too short by more than 0.02 Å. In addition, the calculated dissociation energy of Bi₂, which is larger than experiment by more than 8 kcal/mol, is expected to be strongly affected by spin-orbit coupling effects (see above comments for Bi atom). For the other spectroscopic constants of Bi₂, our present results are considerably more ac-

curate compared to experiment than previous, small basis set RECP CI studies (cf., Ref. 38, and references therein).

The results for the nitrides and oxides in Tables III and IV, respectively, are of very similar quality as the homonuclear diatomics and have similar convergence rates with respect to basis set. The same can also be said for the chlorides shown in Table V. In the latter case, the errors in r_e with respect to experiment with the cc-pV5Z-PP basis sets range from 0.03 to nearly 0.08 Å. This is not unexpected since strong core-valence correlation effects for the group 13 elements should strongly decrease their bond lengths. To a lesser extent, second order spin-orbit effects will also have a non-negligible (but smaller) impact on their spectroscopic constants. In the case of PbO, comparison of the present results with those of Metz *et al.*¹² clearly show that correlation of the semicore d electrons reduces the equilibrium bond length by ~ 0.02 Å. For the chlorides, the TiCl work of Metz *et al.*¹¹ demonstrates that correlation of the $5d$ electrons shortens r_e by up to 0.03 Å, while $5s5p$ correlation contributes an additional -0.02 Å for a total core-valence correlation effect of approximately -0.05 Å on r_e . The remaining error (~ 0.02 Å) can be associated with spin-orbit effects and core-valence correlation involving Cl. The relatively poor agreement with experiment for the dissociation energy of PbO at the CCSD(T)/cc-pV5Z-PP level of theory can be attributed to inaccuracies in removing spin-orbit coupling effects of the Pb atom from the experimental value by just

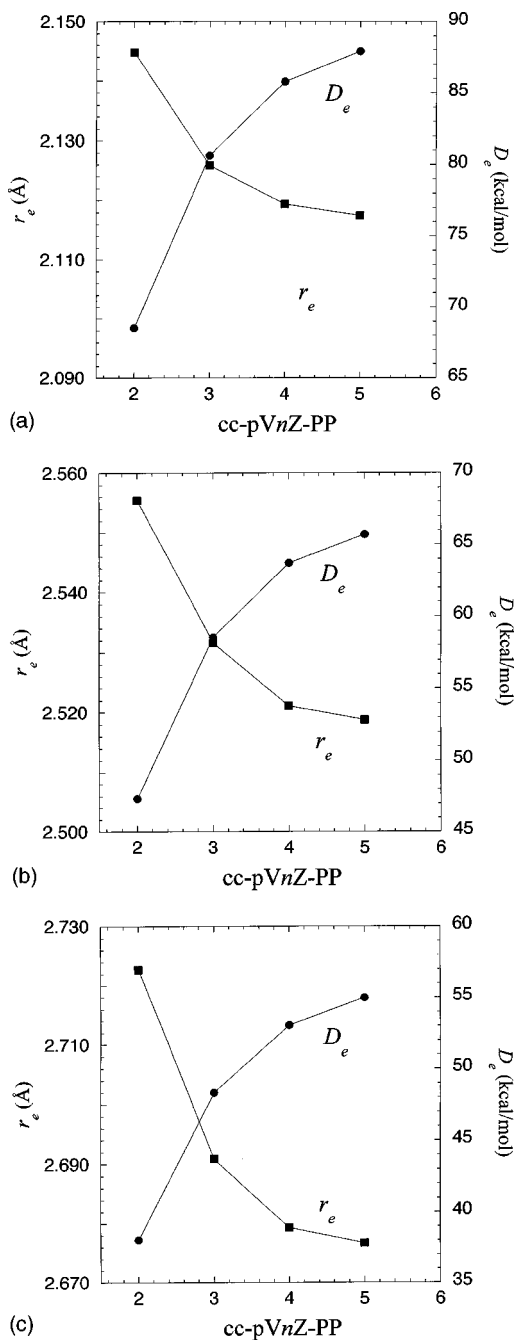


FIG. 6. Convergence of the calculated CCSD(T) equilibrium dissociation energies (D_e) and bond lengths (r_e) as a function of cc-pVnZ-PP basis set for (a) As₂, (b) Sb₂, and (c) Bi₂.

using the j -averaged energy within the 3P manifold (i.e., neglecting second-order effects). The neglect of molecular second-order spin-orbit coupling in the present calculations is also expected to play an important role. These issues are planned to be the subject of a subsequent study. The dissociation energies for both GeO and SnO are within the experimental uncertainties at this level.

Very similar errors with respect to experiment are also observed in Table VI for the hydrides involving the group 13 elements and the calculated spectroscopic constants are nearly converged with basis set at the QZ level. Here again, large core-valence effects are to be expected from the semi-

core d electrons, which should account for most of the errors, particularly in r_e . As shown recently by Zou *et al.*³⁹ the spin-orbit effects on r_e and ω_e for InH are nearly negligible in its ground state, e.g., the equilibrium bond length changes by just -0.001 Å upon inclusion of SO coupling. This effect is expected to increase, however, in the case of TIH to a bond shortening of 0.02 – 0.03 Å (see Ref. 40, and references therein).

For many of the diatomics involving post-3d and -4d elements shown in Tables II–VI, the present cc-pVnZ-PP results, which have been shown in several cases to be nearly identical to all-electron calculations, can also be compared to the work of Martin and Sundermann,¹⁶ who employed large-core relativistic PPs with their new SDB-cc-pVnZ basis sets ($n=T$ and Q) at the CCSD(T) level of theory. For the most part, their SDB-cc-pVTZ results are in good agreement with the cc-pVTZ-PP results of the present work; both their r_e and D_e values are only slightly smaller on average than the present results. Use of their SDB-cc-pVQZ basis sets, however, results in relatively large deviations from the cc-pVQZ-PP values of the present work. For instance, the bond distances of As₂ and AsN are too short by ~ 0.01 Å, while their calculated r_e for Sb₂ is shorter by nearly 0.02 Å. In addition, the dissociation energies calculated with the SDB-cc-pVQZ basis in Ref. 16 are too large for these molecules by 1–3 kcal/mol. The origin of these errors does not lie in the basis sets themselves but the use of large-core pseudopotentials. A detailed comparison of large- and small-core PP's has been presented for various In compounds by Leininger *et al.*,¹⁰ as well as for PbO in the work of Metz *et al.*¹² These studies clearly showed that large core PP's can lead to strong underestimation of r_e values, which is primarily due to the underestimation of Pauli repulsions between the closed shell electrons on one center with the core simulated by the PP on the other center. This would appear to very adequately explain the much shorter bond lengths in the work of Martin and Sundermann¹⁶ compared to those of the present work where only small-core PP's are used.

IV. SUMMARY

Series of correlation consistent basis sets from double- to quintuple- ζ quality have been developed using relativistic small-core pseudopotentials for the post- d group 13–15 elements. Both standard (cc-pVnZ-PP) and augmented (aug-cc-pVnZ-PP) sets are reported. The HF and correlation energies each appear to approach their respective CBS limits both rapidly and systematically in atomic calculations. Numerous diatomic benchmark calculations also demonstrate similar regular convergence behavior in both energies and spectroscopic properties. Comparison to large basis set, all-electron, 1-component relativistic calculations indicate very small errors due to the pseudopotential approximation, typically only ~ 0.002 Å in r_e and less than 0.5 kcal/mol in D_e . Hence these sets should provide a means for calculating accurate relativistic values for a wide range of molecular properties, especially when spin-orbit effects are included. These new basis sets are appropriate for correlation of the valence s and p electrons and hence care should be taken to avoid pseudocore/valence correlation effects from the $(n-1)d$

TABLE III. CCSD(T) total energies and spectroscopic constants calculated for AsN, SbN, and BiN compared to experiment.

Basis ^a	E_{\min} (E_h)	E_{∞} (E_h)	r_e (\AA)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (kcal/mol)
AsN						
cc-pVDZ-PP	-385.866 391	-385.745 101	1.6470	1013.63	5.31	76.11
cc-pVTZ-PP	-385.979 247	-385.812 326	1.6322	1062.74	5.17	104.74
cc-pVQZ-PP	-386.003 734	-385.827 574	1.6265	1070.49	5.07	110.54
cc-pV5Z-PP	-386.011 936	-385.832 231	1.6252	1073.32	5.07	112.77
all-electron:						
cc-pV5Z-DK	-2 313.776 411	-2 313.597 382	1.6264	1071.67	5.06	112.34
Expt. ^b			1.61843	1068.54		116.0±0.5
SbN						
cc-pVDZ-PP	-293.902 774	-293.809 508	1.8805	803.17	5.00	58.53
cc-pVTZ-PP	-293.984 287	-293.866 576	1.8582	858.72	4.56	73.87
cc-pVQZ-PP	-294.009 024	-293.881 447	1.8499	870.36	4.42	80.06
cc-pV5Z-PP	-294.017 121	-293.885 919	1.8475	873.26	4.38	82.33
all-electron:						
cc-pV5Z-DK	-6 531.277 402	-6 531.147 227	1.8502	870.8	4.39	81.69
Expt. ^c			1.8352	864.80	4.75	
BiN						
cc-pVDZ-PP	-268.186 253	-268.115 457	1.9884	690.01	5.51	44.43
cc-pVTZ-PP	-268.263 156	-268.168 458	1.9563	755.98	4.44	59.42
cc-pVQZ-PP	-268.288 647	-268.183 826	1.9447	770.47	4.21	65.78
cc-pV5Z-PP	-268.296 829	-268.188 310	1.9417	773.58	4.13	68.10
all-electron:						
cc-pV5Z-DK	-21 564.924 799	-21 564.816 643	1.9416	774.03	4.15	67.87
Expt. ^d			1.93491	736.57	4.83	

^acc-pVnZ (with cc-pVnZ-PP) or cc-pV5Z-DK (with cc-pV5Z-DK on As) on N.^bReferences 42 and 45.^cReference 46.^dReference 47.

TABLE IV. CCSD(T) total energies and spectroscopic constants calculated for GeO, SnO, and PbO compared to experiment.

Basis ^a	E_{\min} (E_h)	E_{∞} (E_h)	r_e (\AA)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e ^b (kcal/mol)
GeO						
cc-pVDZ-PP	-368.525 911	-368.307 144	1.6606	929.94	4.26	137.28
cc-pVTZ-PP	-368.636 421	-368.392 819	1.6392	979.90	4.39	152.86
cc-pVQZ-PP	-368.666 953	-368.415 687	1.6368	981.54	4.35	157.67
cc-pV5Z-PP	-368.677 176	-368.423 136	1.6359	981.51	4.33	159.41
all-electron:						
cc-pV5Z-DK	-2 172.373 918	-2 172.120 697	1.6373	979.97	4.32	158.90
Expt. ^c			1.62465	985.5	4.29	161±3
SnO						
cc-pVDZ-PP	-288.467 146	-288.293 069	1.8827	768.14	3.88	109.24
cc-pVTZ-PP	-288.567 486	-288.371 029	1.8582	809.20	3.75	123.28
cc-pVQZ-PP	-288.599 369	-288.393 363	1.8527	817.97	3.67	129.27
cc-pV5Z-PP	-288.609 763	-288.400 691	1.8514	817.64	3.63	131.19
Expt. ^c			1.83251	814.6	3.73	134±3
PbO						
cc-pVDZ-PP	-266.930 993	-266.780 875	1.9883	674.02	3.89	94.20
cc-pVTZ-PP	-267.027 070	-266.855 671	1.9598	716.02	3.41	107.55
cc-pVQZ-PP	-267.059 990	-266.878 357	1.9512	727.34	3.31	113.98
cc-pV5Z-PP	-267.070 724	-266.885 824	1.9495	727.29	3.29	116.03
Expt. ^d			1.92181	721.0	3.54	113.9

^acc-pVnZ (with cc-pVnZ-PP) or cc-pV5Z-DK (with cc-pV5Z-DK on Ge) on O.^bAtomic spin-orbit splittings have been removed from the experimental values.^cReferences 42 and 45.^dReference 42.

TABLE V. CCSD(T) total energies and spectroscopic constants calculated for GaCl, InCl, and TlCl compared to experiment.

Basis ^a	E_{\min} (E_h)	E_{∞} (E_h)	r_e (\AA)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e^b (kcal/mol)
GaCl						
cc-pVDZ-PP	-718.112 378	-717.946 231	2.2843	339.93	1.09	104.26
cc-pVTZ-PP	-718.199 520	-718.025 822	2.2410	357.70	1.23	109.00
cc-pVQZ-PP	-718.224 145	-718.046 388	2.2353	358.69	1.23	111.54
cc-pV5Z-PP	-718.232 068	-718.052 830	2.2323	360.42	1.24	112.47
all-electron:						
cc-pV5Z-DK	-2 403.471 922	-2 403.293 179	2.2330	360.27	1.24	112.16
Expt. ^c			2.20169	365.3	1.2	117±3
InCl						
cc-pVDZ-PP	-649.014 304	-648.855 406	2.4901	297.17	0.95	99.71
cc-pVTZ-PP	-649.092 750	-648.928 273	2.4571	307.68	1.01	103.21
cc-pVQZ-PP	-649.116 812	-648.948 039	2.4497	309.52	1.01	105.91
cc-pV5Z-PP	-649.124 591	-648.954 419	2.4465	310.73	1.02	106.78
Expt. ^c			2.40117	317.4	1.01	109±2
TlCl						
cc-pVDZ-PP	-631.307 779	-631.155 776	2.5995	265.87	0.84	95.38
cc-pVTZ-PP	-631.382 678	-631.226 085	2.5713	271.64	0.88	98.26
cc-pVQZ-PP	-631.406 830	-631.246 141	2.5656	273.09	0.88	100.83
cc-pV5Z-PP	-631.414 574	-631.252 616	2.5624	273.99	0.88	101.63
Expt. ^d			2.48483	283.75	0.82	104

^aaug-cc-pVnZ on Cl with cc-pVnZ-PP or aug-cc-pV5Z-DK on Cl with cc-pV5Z-DK on Ga.^bAtomic spin-orbit splittings have been removed from the experimental values.^cReferences 42 and 45.^dReference 42.

TABLE VI. CCSD(T) total energies and spectroscopic constants calculated for GaH, InH, and TlH compared to experiment.

Basis ^a	E_{\min} (E_h)	E_{∞} (E_h)	r_e (\AA)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e^b (kcal/mol)
GaH						
cc-pVDZ-PP	-258.934 721	-258.833 395	1.6883	1588.76	26.42	63.58
cc-pVTZ-PP	-258.956 747	-258.849 572	1.6850	1595.64	27.26	67.25
cc-pVQZ-PP	-258.960 393	-258.851 809	1.6836	1591.77	27.59	68.14
cc-pV5Z-PP	-258.961 316	-258.852 308	1.6837	1588.78	27.64	68.40
all-electron:						
cc-pV5Z-DK	-1 942.790 885	-1 942.681 966	1.6845	1588.17	27.66	68.35
Expt. ^c			1.66015	1603.96	28.42	≤69
InH						
cc-pVDZ-PP	-189.835 444	-189.742 571	1.8674	1473.59	25.00	58.28
cc-pVTZ-PP	-189.850 348	-189.752 023	1.8731	1466.74	24.32	61.70
cc-pVQZ-PP	-189.853 498	-189.753 460	1.8704	1461.79	24.67	62.77
cc-pV5Z-PP	-189.854 455	-189.753 897	1.8704	1458.51	24.46	63.10
Expt. ^d			1.8380	1476.04	25.61	63.6
TlH						
cc-pVDZ-PP	-172.128 895	-172.042 941	1.9414	1376.49	23.36	53.94
cc-pVTZ-PP	-172.141 062	-172.049 836	1.9458	1362.94	22.09	57.25
cc-pVQZ-PP	-172.144 767	-172.051 562	1.9418	1353.99	21.99	58.49
cc-pV5Z-PP	-172.145 872	-172.052 093	1.9415	1349.84	21.96	58.85
Expt. ^d			1.8702	1390.7	22.7	62.2

^acc-pVnZ (with cc-pVnZ-PP) or cc-pV5Z-DK (with cc-pV5Z-DK on Ga) on H.^bAtomic spin-orbit splittings have been removed from the experimental values.^cReferences 45 and 48.^dReference 42.

electrons. Appropriate core-valence basis sets, such as the cc-pwCVnZ sets recently reported for the second row atoms,⁷ will be the subject of a subsequent study.

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