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REGULAR ARTICLE

Core-valence correlation consistent basis sets for second-row atoms (Al–Ar) revisited

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Abstract The augmented tight-*d* cc-pV($n+d$)Z (where n = D, T, Q, 5) basis sets are now the recommended "standard" correlation consistent basis set for second-row atoms. These revised sets, however, do not have a suitable corresponding core–valence basis set series to enable an assessment of core–valence corrections. This is particularly important when such effects are assessed and are used as an additive effect, as is done in composite methods. Thus, there is a need for a new "standard" core–valence series of basis sets for second-row atoms that builds systematically upon the cc-pV($n+d$)Z sets. In this study, we develop the cc-pCV($n+d$)Z basis set series and demonstrate their usefulness through molecular benchmark calculations for a series of second-row systems. These revised core–valence basis sets provide greater consistency in the description of core–valence effects with respect to change in basis set, enabling greater utility of the sets, even for the lower values of n.

Keywords Basis sets · Correlation consistent · Second-row atoms · Al–Ar

1 Introduction

Since their original development by Dunning in 1989, the correlation consistent basis sets [1] have seen widespread utility in thousands of studies. The popularity of these basis sets stems from their unique construction which entails a "consistent" improvement in the description of electron correlation [2]. This construction has enabled a systematic improvement in the description of numerous molecular properties as the basis set size is increased. The systematic nature of the correlation consistent basis set series has enabled a variety of simple formulas to be used to estimate the complete basis set (CBS) limit—the limit at which no further improvement in basis set will ameliorate upon the results. In the approximate solution to the Schrödinger equation, this has enabled the errors arising from choice of method and errors arising from choice of a basis set to be disentangled, thus allowing the *intrinsic error*, the error arising from choice of method, to be understood. In turn, this has enabled a well-developed hierarchy of the performance of ab initio methods to evolve. As well, the combination of a method such as coupled cluster theory with single, double, and quasiperturbative triple excitations [CCSD(T)] with the correlation consistent basis sets has allowed the prediction of molecular properties within "chemical accuracy" (e.g., dissociation energies within 1 kcal/mol of reliable, well-established results from experiment) [3–17].

Though the focus of the work described herein is upon core–valence effects, a thorough description of the cc-pV($n+d$)Z basis sets, which leads to the present work is in order. In 1995, Bauschlicher and Partridge [18] observed an unusually large (∼6 kcal/mol) deviation from the experimentally established atomization energy of SO_2 in comparison to their CCSD(T) calculated value at the CBS limit. For the atomization energy of SO_2, Bauschlicher and Partridge noted that the energy computed using the aug-cc-pVTZ basis set was much poorer (∼10 kcal/mol) than that obtained using the 6-311+G(3df,2p) basis set. This difference was attributed to the lack of high exponent (tight) *d* functions in the aug-cc-pVTZ basis set. This study was the first to show that an additional tight-*d* function significantly impacts the

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dissociation energy of SO_2, and suggested that additional high exponent functions would further improve the dissociation energy. Following this work, Martin [19] noted a significant deviation from experiment in the dissociation energy of SO, and investigated the impact of the addition of a series of large exponent higher angular momentum functions to the correlation consistent basis sets. In a later study, Martin and Uzan observed that such deviations also occurred for other second-row species, such as SiO and Cl_2, and again, noted that these deviations could be remedied by the inclusion of additional tight basis functions [19]. It should be noted that the extrapolations utilized in these earlier studies did not include cc-pVDZ results. As a result of this omission, the error at the CBS limit was exacerbated. Much smaller errors would have been obtained if the cc-pVDZ results had been included in the extrapolation schemes.[22] However, this extreme sensitivity of the CBS limit to the inclusion or exclusion of the cc-pVDZ results did further exemplify a convergence issue in the cc-pVnZ sets for the second-row atoms [20].

Dunning et al. [20] have cautioned that the addition of any new functions to a basis set, however arbitrary, will result in the improvements to the total energy, and possibly to the dissociation energy, as the effects of correlation are larger in molecules than in atoms [20]. In light of this, and the obvious deficiencies noted in the basis sets, Dunning et al. [20] re-evaluated the construction of the standard cc-pVnZ basis sets for second-row atoms. By comparing D_e of O_2 to SO, they noted two possible problems in the construction of the valence d-sets, which could affect the convergence behavior in second-row systems: (1) a near duplication of exponents in the (3d) and (4d) sets; and (2) a deficiency in the early members of the d sets needed for the description of core polarization effects and valence orbital correlation effects. To remedy these problems, modifications to the cc-pVnZ basis sets were made that included the addition of a single tight-d basis function at each basis set level and a re-optimization of all the d-functions in order to provide a systematic expansion of the valence and outer core regions. During the optimization of the new sets of d functions, it was also noted that the even-tempered expansion for the d-sets was no longer adequate.

The modified basis sets, known as the cc-pV(n+d)Z and aug-cc-pV(n+d)Z series of basis sets, successfully addressed the differences in the convergence behavior of D_e for O_2 and SO. Further benchmarks, on Si_2, PN, and AlCl in Dunning's initial study, also demonstrated that calculated molecular properties, such as D_e, converge more quickly to the CBS limit. Wilson et al. [21] have shown that the augmented tight-d basis sets have significant impact on the structure and energetics of SO_2. In fact, r_e (SO) in SO_2 at the cc-pV(T+d)Z level is comparable to the bond distance determined using cc-pV5Z (1.4398 and 1.4348 Å, respectively). The improvement of the convergence behavior in the dissociation energy of SO_2 resulted in a reduction of the error in the three-point CBS limit (TZ, QZ, 5Z) from 6.0 kcal/mol for the cc-pVnZ set to less than 1.0 kcal/mol for the cc-pV(n+d)Z sets when the zero-point energy (ZPE) correction was included. Also, in a study of SO_3 [22], the effect of a single tight-d function on atomization energy was an astounding 25.27 kcal/mol at the double-ζ level and 14.32 kcal/mol at the triple-ζ level. These benchmark studies, as well as others [23–26], have illustrated the importance of the cc-pV(n+d)Z and aug-cc-pV(n+d)Z sets. These sets have also been instrumental in many recent studies in which accurate molecular structure and energetics are crucial [27–51].

In the majority of electronic structure calculations, the frozen–core approximation is utilized due to both computational efficiency and interest in the chemistry largely associated with the valence electrons. However, often for accurate descriptions of structural (<0.01 Å)and energetic (<1.0 kcal/mol) properties, the inclusion of core–core and core–valence correlation is necessary [4,6,10]. Such all-electron calculations should not be performed utilizing basis sets optimized for valence-only correlated calculations, as they do not provide a flexible description of the core orbitals [52]. Rather, basis sets explicitly designed to describe the core–core and core–valence correlation should be used. Woon and Dunning [53] developed the first systematic series of basis sets, the correlation consistent polarized core valence *n-zeta* (cc-pCVnZ) basis sets, designed for describing the core–core and core–valence contribution to the total correlation energy. In the development of the core basis functions for first-row atoms (B–Ne), the exponents of the core functions were optimized in the presence of the cc-pVnZ valence sets to minimize (i.e., the largest negative value) the core–core and the core–valence correlation energy, using the configuration interaction with single and double excitations (CISD) method. Peterson and Dunning [54] later developed cc-pCVnZ sets for second-row atoms (Al–Ar) in a manner akin to that utilized for the development of basis sets for first-row atoms, thereby adding ($1s1p1d$) to cc-pVDZ, ($2s2p2d1f$) to cc-pVTZ, ($3s3p3d2f1g$) to cc-pVQZ, and ($4d3f2g1h$) to cc-pV5Z. (For cc-pCV5Z, new core s and p functions were not optimized; rather, the ($20s12p$) primitive HF sets were recontracted to [$11s10p$], see [54] for further discussion.) Peterson and Dunning found [54] that the convergence of the core–valence contribution to the total correlation energy was slower than that of core–core correlation when the cc-pCVnZ basis sets were used. As a result of this observation, they also developed the *weighted* core–valence correlation consistent basis sets (cc-pwCVnZ) for first- and second-row atoms [54]. For these sets, the exponents of the core functions were optimized to favor the core–valence contribution by weighting the core–core correlation term, in order to increase the rate of convergence of the core–

valence correlation. Peterson and Dunning discovered that the inclusion of a small fraction of the core–core correlation must be used in order to maintain systematic convergence behavior in the correlation energy.

Basis sets such as the cc-pCV*n*Z set, which include extra functions specifically to describe the core region in all-electron calculations, dramatically increase the cost (i.e., time, disk space, and memory) of calculations. Because of this significant increase in computational cost, a common approach to account for core–valence effects is to treat them as additive effects, rather than completing full geometry optimizations using larger core–valence basis sets. In the additive treatment of core–valence effects, single-point calculations are performed at the optimized geometry determined from a frozen–core calculation using a valence basis set. These single-point calculations often utilize a lower basis set ζ-level than that was used in the frozen–core calculations. The core–valence effect, ΔE_{CV}, can be defined as

$$\Delta E_{\mathrm{CV}} = E\ (\text{all-electron}) - E\ (\text{frozen–core}), \tag{1}$$

where E (all-electron) represents the total energy obtained from an all-electron calculation, and E (frozen–core) represents the total energy obtained from a frozen–core calculation. This approach can provide a good approximation of the core–valence effects, provided that the change in geometry due to the core–valence correlation is minimal, and that the core–valence effect does not change dramatically from one basis set level to another. The most rigorous way to determine ΔE_{CV} is to utilize a core–valence basis set for both the all-electron and the frozen–core energies; however, a common approach for assessing ΔE_{CV} for composite methods is to utilize a core–valence basis set for the all-electron energy and a valence basis set for the frozen–core energy. Many recent studies have assessed core–valence effects at the triple-ζ level and have utilized this data as additive corrections to their frozen–core calculations performed using higher ζ-level basis sets [5,6,55–68]. Composite approaches which use ΔE_{CV} as an additive effect include G3 theory [69,70], W*n* theories [71], CBS-Q and CBS-QB3 [72,73], and ccCA [74,75], though only the W*n* and ccCA approaches have used the correlation consistent basis sets.

As described earlier, the cc-pV*n*Z basis set series has served as the foundation for the development of the core–valence basis sets, cc-pCV*n*Z. However, for the augmented tight-*d* basis sets (cc-pV(n+d)Z) [20], there are no corresponding core–valence sets. Rather, for second-row atoms, the standard core–valence basis sets are still used. However, there are deficiencies which arise from this, which suggest the need for modified core–valence basis sets that are compatible with the augmented tight-*d* valence sets. First, there are two d-functions in both the cc-pV(D+d)Z and the cc-pCVDZ sets. Core–valence sets systematically build upon valence basis sets at all angular momentum levels; thus, this equivalent number suggests that the core–valence sets may be deficient in the number of d-functions at each basis set level. Second, it is expected that D_e from valence-only correlated calculations with the cc-pV(n+d)Z basis sets would be smaller than D_{e} determined from all-electron calculations with the cc-pCV*n*Z basis sets. However, as discussed further in Sect. 3, this does not occur for each basis set level of these two series of basis sets.

Because of the superiority and recommended use of the cc-pV(n+d)Z basis sets rather than the cc-pV*n*Z sets for frozen–core calculations, the aim of this paper is to develop core–valence basis sets built upon the cc-pV(n+d)Z valence sets for use in all-electron calculations. Using the modified sets developed in the present study, benchmark calculations have been performed to predict the D_0 and bond lengths of SO, SO_2, SO_3, S_2, AlCl, PN, and Si_2 to illustrate the utility of these basis sets.

2 Methodology

The subsequent subsections outline two schemes for the construction of core–valence sets based upon the cc-pV (n+d)Z valence sets for second-row atoms. In order to maintain consistency with the development of the original correlation consistent core–valence sets for second-row atoms, the total number of core-d functions beyond the cc-pV(n+d)Z valence-d sets in the new cc-pCV(n+d)Z sets should be 1d (for n = D), 2d (for n = T), 3d (for n = Q), and 4d (for $n = 5$). The optimization of these new core-d functions should also provide a systemic improvement upon the electron correlation energy and prediction of molecular properties computed with cc-pV(n+d)Z. This improvement is expected to be similar to the improvement seen when using the cc-pCV*n*Z sets for all-electron calculations as compared with the cc-pV*n*Z sets for valence-only calculations. For the optimization of the d-exponents, the CISD method was used. The reference wavefunction for the CISD calculations was obtained by state-averaging any degenerate ground states for the atoms. In the all-electron calculations, only 1 s (K shell) was frozen for the second-row atoms, which is generally not of chemical interest and contributes very little to the total electron correlation. This was also the procedure used in the original development of the cc-pCV*n*Z sets for the second-row atoms.

The MOLPRO 2002.6 quantum chemistry software suite was used throughout this study [76].

2.1 General basis set considerations

As mentioned previously, relative to the cc-pV(n+d)Z basis sets, the cc-pCV*n*Z basis sets are deficient by one core-d function at each basis set level. So, in the revision of the core–

valence sets, an additional core-*d* function was included in the sets, and all of the core-*d* functions were optimized for each ζ-level. In order to maintain consistency with the previous core–valence correlation consistent basis sets the new core-*d* set was optimized so that the sum of the core–core (LL) and core–valence (LM) correlation was minimized. In other words, the difference in energy between an all-electron CISD and valence-only CISD calculation

$$\Delta E_{\mathrm{corr}} = E_{\mathrm{CISD}}(\mathrm{LL}+\mathrm{LM}+\mathrm{MM}) - E_{\mathrm{CISD}}(\mathrm{MM}). \qquad (2)$$

is minimized. Throughout this study, the core *d* exponents in the basis set were generated by optimizing α and β parameters in an even-tempered expansion, where $\zeta_i = \alpha\beta^{i-1}$ (ζ is the basis set exponent and i represents an index running over the number of Gaussian primitives). The remaining (s, p, f, g, h) core functions were unaltered and were obtained from the cc-pCV*n*Z basis sets. Spherical basis functions were used throughout.

2.2 Optimization scheme 1

The additional core-*d* functions needed to create revised core–valence basis sets should not simply be added to the cc-pCV*n*Z sets. Such an approach would not provide the optimal *d* functions, as these core-*d* functions are optimal for the standard cc-pV*n*Z basis sets, not for the cc-pV$(n+d)$Z sets, which should serve as the base for the revised core–valence sets. Therefore, in the presence of the valence functions from the cc-pV$(n+d)$Z sets (including the tight-*d* function which are referred to as ζ_0), all of the core-*d* functions (herein referred to as ζ_1, ζ_2, ζ_3 ...) were reoptimized including the additional core-*d* function. Overall, for the double-, triple-, and quadruple-ζ basis sets, the optimization resulted in core-*d* functions which had higher exponents than the tight-*d* function, ζ_0. These functions are shown in Fig. 1a for sulfur.

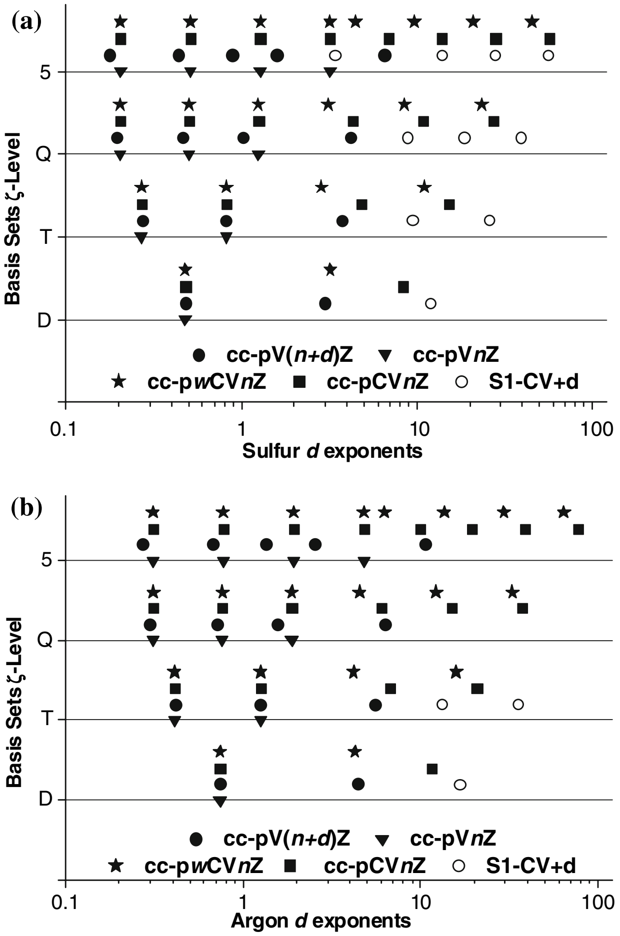

Fig. 1 The optimized core-*d* exponents for (**a**) sulfur and (**b**) argon using scheme 1 (S1-CV+d) outlined in Sect. 2.2 are plotted as *open circles*. The valence-*d* exponents from cc-pV*n*Z and cc-pV$(n+d)$Z and the core-*d* exponents from cc-pCV*n*Z and cc-p*w*CV*n*Z are plotted with *solid symbols* for comparison

Generally, augmenting the valence basis sets with core functions produces exponents with higher values than those of the valence sets. At the quintuple-ζ level, however, the optimal ΔE_{corr} resulted in a smaller ζ_1 exponent than the ζ_0 exponent. This arises, in part, due to the saturation of the *d*-space at the quintuple-ζ level when nine *d*-functions are present, and to the large ζ_0 function (6.510), which is significantly in the core region. To circumvent a linear dependence problem, which occurred for the ζ_2 and ζ_0 functions upon optimization of the core-*d* exponents, the determination of the spacing, β, between exponents was changed. Normally, β is defined as the spacing between the first two core-*d* exponents, ζ_1 and ζ_2. For the quintuple-ζ set, the tight-*d* exponent (ζ_0) from the cc-pV(5+d)Z set remains fixed as before, while the first core-*d* exponent (ζ_1) was optimized so that it was smaller than the ζ_0 function, and the β spacing was redefined as the spacing between the ζ_1 and the ζ_0 exponent. The second core-*d* exponent (ζ_2) was given a value of $\alpha\beta^2$, so that the ζ_1 and ζ_2 exponents would straddle the fixed ζ_0 tight-*d* function. The value of the third core-*d* function (ζ_3) was $\alpha\beta^3$, and the value of the ζ_4 function was $\alpha\beta^4$. This scheme was chosen for all of the quintuple-ζ core-*d* sets in scheme 1.

The cc-pV$(n+d)$Z valence-*d* functions were used as the base to build core-*d* functions. A non-even-tempered spacing of the *d*-functions was utilized, as it was needed to expand both the valence and outer core regions [20]. The non-even-tempered approach used to determine the valence-*d* and tight-*d* exponents in the cc-pV$(n+d)$Z basis sets lead to difficulties in the optimization of core-*d* functions using scheme 1. This was discussed previously, and can be seen in Fig. 1a at the quintuple-ζ level. Another example can be shown by the difficulties encountered in optimizing core-*d* functions in the presence of the valence-*d* set from cc-pV$(n+d)$Z for argon, as shown in Fig. 1b. In this case, the scheme 1 optimization resulted in linear dependency problems for the ζ_0 and ζ_1 exponents at the quadruple-ζ level. Straddling the ζ_0 function, as done at the quintuple-ζ level, by changing the normal β spacing, was unsuccessful as well, due again to the linear dependency of the ζ_1 and ζ_0 exponents. These inconsistencies in the construction of the core-*d* exponents led to a second optimization approach (scheme 2).

2.3 Optimization scheme 2

Because of the complications arising from the scheme 1 optimization, the focus of this scheme was to re-establish an even-tempered expansion throughout the valence and core regions. This entailed a reoptimization of the tight-*d* exponent with the set of core-*d* functions. It must be noted, while optimizing the cc-pV(n+d)Z sets, a few issues were encountered in optimizing the tight-*d* function at the double- and triple-ζ levels. As discussed in [20], the initial optimization of the 3*d* set exponents for cc-pV(T+*d*)Z, resulted in *d*-function exponents in only the valence space without a needed tight-*d* function. Therefore, in the final approach used in [20], only the tight-*d* function was optimized. At the cc-pV(D+*d*)Z level, the optimized tight-*d* exponent was much smaller than the corresponding triple- or quadruple-ζ tight-*d* functions. This large change in the tight-*d* exponent at the cc-pV(D+*d*)Z level is thought to be due to the small number of *d*-functions present for the description of both the valence and outer core regions. Subsequently, the tight-*d* function in the cc-pV (D+*d*)Z basis set was estimated from a ratio of the triple- and quadruple-ζ tight-*d* functions. (See [20] for further details on optimization of tight-*d* exponents in cc-pV(n+d)Z.) It is thought that the challenges faced during the optimization of the original tight-*d* function should not arise while optimizing the tight-*d* exponent together with the core-*d* functions Fig. 2.

In light of the problems encountered in scheme 1, in scheme 2 the original cc-pVnZ sets were used as the base for constructing new ζ_0 and core-*d* sets, since the cc-pVnZ sets contain an even-tempered set of *d* functions. A simple analysis of Fig. 1 shows that ζ_0 from cc-pV(n+d)Z is generally located in the region between the ζ_1 core-*d* exponents of cc-pwCVnZ and cc-pCVnZ. Optimizing the ζ_0 function with the core-*d* functions allowed more flexibility in the description of the core region, which lowered the ΔE_{corr} as compared to scheme 1. For argon at the double-ζ level, scheme 2 results in a lower ΔE_{corr} by $1.829\, mE_h$ in comparison to ΔE_{corr} obtained from optimization scheme 1. Optimization of the ζ_0 exponent and the set of core-*d* functions ($\zeta_1, \zeta_2, \zeta_3, \zeta_4$) with scheme 2 did not lead to any inconsistencies at the various basis set levels. Furthermore, at the double-ζ level, the addition of a core-*d* function caused the ζ_0 exponent to optimize in the core region without estimating the exponent, as discussed previously.

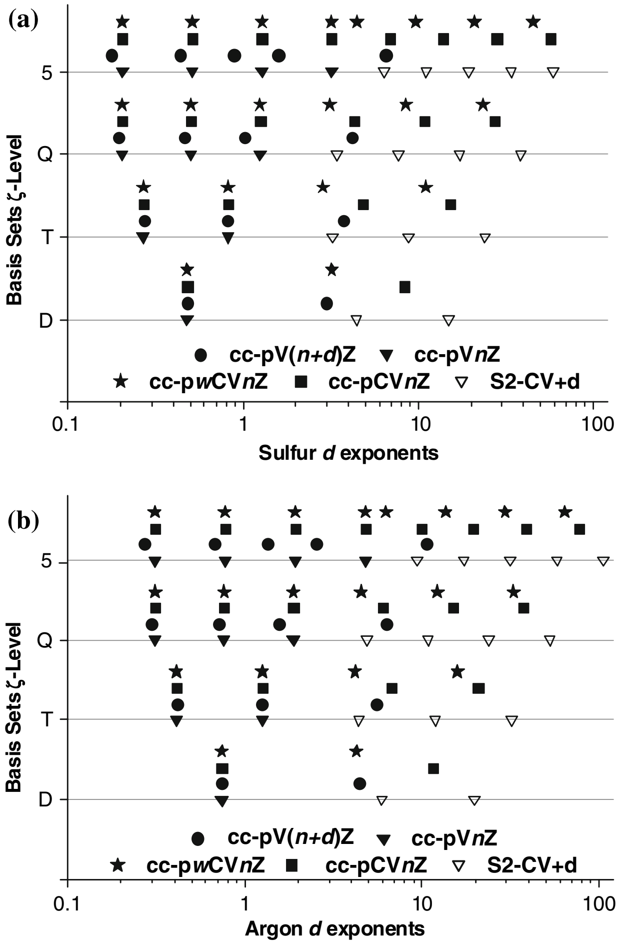

Fig. 2 The optimized core-*d* exponents for **a** sulfur and **b** argon using Scheme 2 (S2-CV+d) outlined in Sect. 2.3 are plotted as *open triangles*. The valence-*d* exponents from cc-pVnZ and cc-pV(n+d)Z and the core-*d* exponents from cc-pCVnZ and cc-pwCVnZ are plotted with *solid symbols* for comparison

2.4 Mixed approach: optimization scheme 3

Further analysis of scheme 2 during the molecular benchmark studies (discussed in Sect. 3) suggested deficiencies in the scheme. In particular, D_e computed while using cc-pCV (D+*d*)Z did not improve upon the cc-pV(D+*d*)Z valence-only values for all of the molecules tested. Closer inspection of the ζ_0 functions in scheme 2 revealed that at the double-ζ level, the ζ_0 exponent does not follow the general trend in which the exponents become more diffuse as the basis set size is decreased. To illustrate, for sulfur the exponents are 6.386, 3.434, and 3.239 for quintuple- quadruple- and triple-ζ, respectively, whereas for double-ζ, the exponent is 4.435. At the double-ζ level the ζ_0 exponent was too far in the core region. This was not surprising due to the small number of *d* functions at the double-ζ level. As well, problems were encountered in the optimization of the tight-*d* (ζ_0) exponent during the development of the cc-pV(D+*d*)Z sets [20]. For scheme 2, this inconsistency in the description of the valence and core regions only occurred at the double-ζ level. Even though the scheme 2 cc-pCV(D+*d*)Z basis set was an improvement over the cc-pCVDZ set, it was still not adequate for the description of molecular properties in all-electron calculations, as it did not improve over the cc-pV(D+*d*)Z valence-only calculations. Therefore, a mixed scheme of scheme 1 and 2 (referred to as scheme 3) was chosen, since scheme 1 did improve upon the cc-pV(D+*d*)Z valence-only calculated molecular properties and ΔE_{corr} as compared to cc-pCVDZ. Scheme 3 used the optimization approach from scheme 1 for the double-ζ basis set which is comprised the newly optimized ζ_1 core-*d* function and the valence-*d* set from cc-pV(D+*d*)Z. The triple-, quadruple-, and quintuple-ζ *d*-exponents were optimized as in scheme 2.

The exponents for the new *d*-functions in cc-pCV(n+d)Z are listed in Table 1. For each atom, the cc-pCV(n+d)Z sets resulted in a lowering of ΔE_{corr} as compared with the cc-pCV*n*Z sets. This is shown in Fig. 3 for sulfur and argon. Also, the convergent behavior of the core–valence correlation energy of the atoms was improved with the inclusion of the additional *d*-function, and is similar to the improvement seen in using cc-pV(n+d)Z valence sets as opposed to the standard cc-pV*n*Z sets.

Table 1 Optimized tight-*d* (ζ_0) and core-*d* (ζ_1, ζ_2, ζ_3, ζ_4) exponents for the second-row atoms (Al–Ar)

Atom	Set	ζ_0	ζ_1	ζ_2	ζ_3	ζ_4
Al	D[a]	0.190	5.938			
	T	1.795	4.992	13.883		
	Q	1.665	3.893	9.100	21.273	
	5	2.897	5.579	10.744	20.690	39.845
Si	D	0.275	7.867			
	T	2.251	6.186	16.999		
	Q	2.266	5.165	11.773	26.833	
	5	4.289	7.958	14.768	27.403	50.849
P	D	0.374	10.056			
	T	2.750	7.504	20.479		
	Q	2.904	6.515	14.618	32.800	
	5	5.429	10.017	18.481	34.097	62.909
S	D	0.481	11.880			
	T	3.239	8.818	24.005		
	Q	3.434	7.681	17.183	38.439	
	5	6.504	12.039	22.284	41.247	76.348
Cl	D	0.603	14.099			
	T	3.846	10.395	28.095		
	Q	4.136	9.185	20.399	45.304	
	5	7.599	14.046	25.964	47.995	88.719
Ar	D	0.739	16.523			
	T	4.424	11.938	32.214		
	Q	4.882	10.784	23.819	52.612	
	5	9.377	17.195	31.531	57.819	106.022

[a] All ζ_0 values at the double-ζ level are from [20]

3 Results

In order to assess the impact of the cc-pCV(n+d)Z basis sets, benchmark calculations have been performed using CCSD(T) [77,78] (and open-shell systems were treated with restricted open-shell RCCSD(T) as implemented in MOLPRO). In these calculations, 1*s* orbital was frozen for the second-row atoms, while no orbitals were frozen for the first-row atoms. The calculated D_0, which is shown in Table 3, included the ZPE correction at each basis set level from CCSD(T) frequency computations. The CBS limit was found using the dissociation energy determined at each basis set level (n = D, T, Q, 5) and the Feller exponential extrapolation [3]. In Table 3, the change in D_0, arising from the use of the tight-*d* sets, namely, $\Delta D_0(+d)$, has been tabulated for the valence-only and all-electron calculations.

The benchmark molecules (SO, SO_2, S_2, AlCl, PN, Si_2) were chosen due to their use in earlier performance studies of the correlation consistent basis sets [20,21,54]. In addition, SO_3 was chosen as it has been considered a benchmark for computational thermochemistry [79], although all-electron optimization of this molecule with CCSD(T) at the quintuple-ζ level with nearly 700 basis functions is quite computationally demanding. The cc-pCV(n+d)Z computed bond lengths provided in Table 2 can be compared to the cc-pCV*n*Z bond lengths. (It should be noted that prior calculations have been done for S_2, Si_2, and PN species using CCSD(T) and the cc-pCV*n*Z basis sets. Our results are mÅ shorter from those reported in [54] because UCCSD(T) was used in open-shell cases in the previous study and more strict energy and geometry thresholds were implemented in the current study than provided by the default in MOLPRO, which was used in the previous study.) The changes in the calculated bond lengths due to the additional augmented core-*d* function are listed, namely, $\Delta r(+d)$. With both series of core–valence basis sets, the bond lengths converge rapidly to the CBS limit. Overall, there is a slight shortening of the bond when the new cc-pCV($n + d$)Z basis sets are used instead of the cc-pCV*n*Z basis sets. This is most notable for SO_2, where the S–O bond length is shortened by 0.0244 Å, and is similar to the $\Delta r(+d)$ found for the valence basis sets (0.0285 Å) [21]. For this test suite the average bond length changed by -0.02 Å when the cc-pCV(D+*d*)Z basis sets are used instead of the cc-pCVDZ basis sets.

The dissociation energies reported in Table 3 contain ZPE corrections, which were not included in the majority of the earlier work. CCSD(T)/cc-pV*n*Z and cc-pV(*n*+d)Z calculations have been previously performed on all of the molecules [20,21], while CCSD(T)/cc-pCV*n*Z benchmark studies have

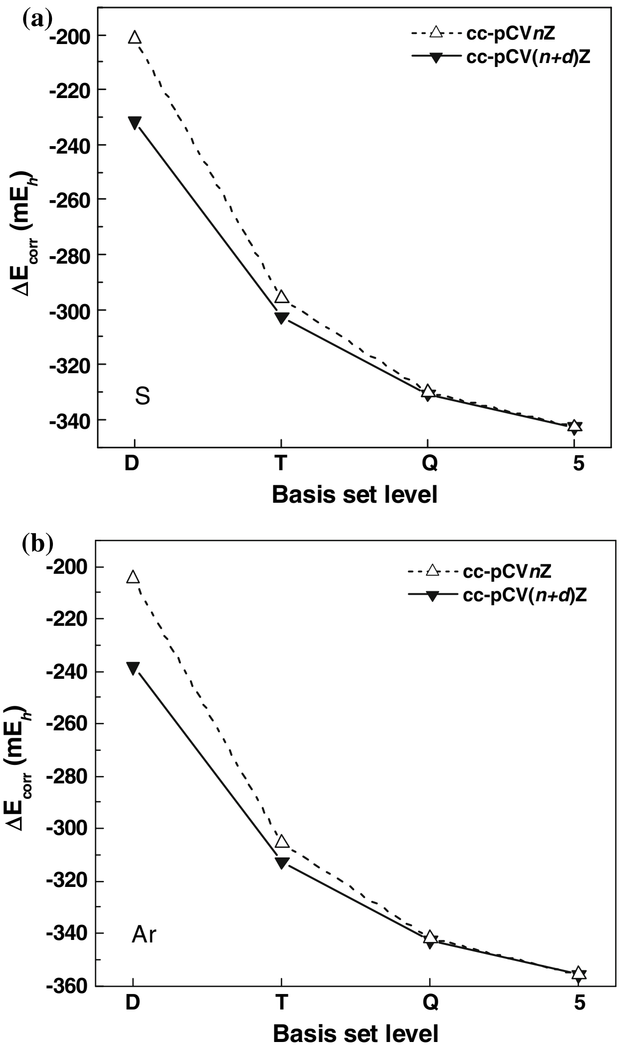

Fig. 3 Comparison of the ΔE_{corr} from the cc-pCV(n+d)Z and cc-pCVnZ basis sets for **a** sulfur and **b** argon using CCSD(T)

Table 2 Optimized geometry (bond lengths in Å) for SO, SO_2, SO_3, S_2, AlCl, PN, and Si_2

Molecule	$n=$	cc-pCVnZ	cc-pC(n+d)Z	$\Delta r(+d)$
SO	D	1.5313	1.5134	−0.0179
	T	1.4895	1.4874	−0.0021
	Q	1.4815	1.4814	0.0000
	5	1.4791	1.4791	0.0000
	Expt.[a]		1.4810	
SO_2	D	1.4820	1.4569	−0.0251
	T	1.4386	1.4360	−0.0026
	Q	1.4340	1.4339	−0.0001
	5	1.4329	1.4329	0.0000
	Expt.[b]		1.4321	
SO_3	D	1.4635	1.4406	−0.0229
	T	1.4247	1.4224	−0.0023
	Q	1.4180	1.4179	−0.0001
	5	1.4166	1.4166	0.0000
	Expt.[c]		1.4173	
S_2	D	1.9329	1.9153	−0.0176
	T	1.9025	1.9007	−0.0018
	Q	1.8911	1.8910	−0.0001
	5	1.8879	1.8879	0.0000
	Expt.		1.8892	
AlCl	D	2.1789	2.1550	−0.0239
	T	2.1442	2.1425	−0.0017
	Q	2.1334	2.1333	−0.0001
	5	2.1308	2.1308	0.0000
	Expt.		2.1301	
PN	D	1.5214	1.5109	−0.0104
	T	1.4990	1.4972	−0.0018
	Q	1.4915	1.4914	−0.0001
	5	1.4898	1.4898	0.0000
	Expt.		1.4909	
Si_2	D	2.2907	2.2775	−0.0132
	T	2.2578	2.2562	0.0016
	Q	2.2457	2.2455	0.0002
	5	2.2430	2.2430	0.0000
	Expt.		2.2460	

The change in bond length due to the augmented-d basis set is listed as $\Delta r(+d)$

[a] All diatomic values are from [82]

[b] From [83–85]

[c] From [86]

been done on Si_2, S_2, and PN [54]. CCSD(T)/cc-pVnZ and cc-pV(n+d)Z benchmarks on SO_2 and SO_3 were obtained from the earlier work by Dunning and Wilson, and this earlier work did include ZPE corrections [21,22,80].

As shown in earlier studies [20–22,24,80], for valence-only (cc-pVnZ and cc-pV(n+d)Z) calculations, the augmented tight-d sets improve the prediction of D_0 for all basis set levels and all molecules studied. This improvement ($\Delta D_0(+d)$) for the valence-only calculations is most noticeable at the double-ζ level and is most significant for S–O bonded systems (4.235, 15.679, 25.272 kcal/mol for SO, SO_2, and SO_3 respectively) as shown in Table 3. Calculating D_0 with the all-electron basis set cc-pCVnZ improves upon the standard cc-pVnZ (valence-only) values; however, at the double-ζ level, the valence-only cc-pV(D+d)Z basis set provides a better prediction of D_0 for all of the systems than the cc-pCVDZ set provides. For example, D_0 of SO_3 is 261.062 kcal/mol at the cc-pV(D+d)Z level, while it is only 241.606 kcal/mol at the cc-pCVDZ basis set level, an astounding ~20 kcal/mol lower. Because D_0 obtained while using the cc-pV(D+d)Z basis set does not include the contribution of the core and core–valence correlation, yet resulted in a larger D_0 than was obtained with the all-electron cc-pCVDZ

Table 3 Computed D_0 (in kcal/mol) for SO, SO_2, SO_3, S_2, AlCl, PN, and Si_2 using CCSD(T)

Molecule	$n =$	cc-pCVnZ	cc-pCV(n+d)Z	$\Delta D_0(+d)$	cc-pCVnZ	ΔE_{CV}	cc-pCV(n+d)Z	ΔE_{CV}	$\Delta D_0(+d)$
SO	D	94.698	98.933	4.235	96.042	1.345	99.599	0.666	3.557
	T	112.871	115.437	2.566	115.796	2.925	116.235	0.798	0.439
	Q	118.762	120.273	1.511	120.909	2.147	120.918	0.645	0.009
	5	121.955	122.285	0.331	122.860	0.905	122.861	0.575	0.001
	CBS limit								
	DT	120.523	122.386	1.863	124.113	3.590	123.239	0.853	−0.874
	TQ	123.061	123.802	0.741	124.641	1.580	124.336	0.534	−0.305
	Q5	125.304	124.397	−0.907	124.906	−0.399	124.899	0.502	−0.007
	DTQ	121.588	122.277	0.690	122.695	1.107	122.753	0.475	0.058
	DTQ5	123.109	122.896	−0.213	123.285	0.176	123.381	0.485	0.096
	Expt.[a]						124.4		
SO_2	D[b]	184.704	200.383	15.679	188.500	3.796	201.702	1.319	13.201
	T	228.290	237.347	9.057	237.707	9.417	239.314	1.967	1.607
	Q	242.525	247.605	5.080	249.278	6.753	249.316	1.711	0.037
	5	250.794	251.835	1.041	253.237	2.443	253.239	1.404	0.002
	CBS limit								
	DT	246.642	252.911	6.269	258.426	11.784	255.150	2.239	−3.275
	TQ	252.913	255.091	2.178	257.722	4.810	256.614	1.524	−1.108
	Q5	259.470	256.273	−3.197	257.390	−2.079	257.355	1.082	−0.035
	DTQ	249.429	251.545	2.116	252.835	3.407	252.939	1.394	0.104
	DTQ5	253.816	252.923	−0.893	253.920	0.104	254.152	1.229	0.231
	Expt.[c]						255.0		
SO_3	D	235.790	261.062	25.272	241.606	5.816	263.032	1.970	21.427
	T	299.320	313.636	14.316	314.200	14.880	316.725	3.089	2.525
	Q	319.690	327.694	8.004	330.343	10.653	330.404	2.710	0.061
	5	331.840	333.374	1.534	335.604	3.764	335.603	2.229	−0.001
	CBS limit								
	DT	326.069	335.772	9.703	344.765	18.696	339.332	3.560	−5.433
	TQ	334.555	337.952	3.397	342.123	7.568	340.385	2.433	−1.738
	Q5	344.588	339.333	−5.254	341.124	−3.463	341.059	1.725	−0.066
	DTQ	329.300	332.813	3.513	334.959	5.659	335.080	2.267	0.121
	DTQ5	336.040	334.676	−1.364	336.373	0.333	336.675	1.999	1.526
	Expt. [c]						337.1		
S_2	D	80.661	84.046	3.385	82.017	1.356	84.877	0.831	2.860
	T	92.303	94.295	1.992	94.677	2.374	94.971	0.676	0.293
	Q	97.670	98.941	1.271	99.582	1.912	99.598	0.657	0.016
	5	100.494	100.767	0.273	101.308	0.814	101.311	0.544	0.003
	CBS limit								
	DT	97.205	98.610	1.405	100.008	2.803	99.221	0.611	−0.788
	TQ	101.587	102.331	0.744	103.162	1.574	102.975	0.643	−0.187
	Q5	103.457	102.683	−0.774	103.119	−0.338	103.108	0.425	−0.011
	DTQ	102.260	102.793	0.533	102.684	0.424	103.514	0.721	0.830
	DTQ5	102.886	102.340	−0.545	102.456	−0.430	102.851	0.510	0.395
	Expt. [a]						101.8		
AlCl	D	107.441	109.132	1.690	108.120	0.679	111.046	1.914	2.926
	T	115.763	116.420	0.657	116.583	0.820	116.654	0.234	0.071
	Q	119.339	119.774	0.434	120.141	0.801	120.152	0.378	0.011
	5	120.858	120.958	0.100	121.299	0.441	121.300	0.342	0.001

Table 3 continued

Molecule	$n =$	cc-pCVnZ	cc-pCV(n+d)Z	$\Delta D_0(+d)$	cc-pCVnZ	ΔE_{CV}	cc-pCV(n+d)Z	ΔE_{CV}	$\Delta D_0(+d)$
	CBS limit								
	DT	119.266	119.488	0.222	120.146	0.880	119.015	−0.474	−1.131
	TQ	121.950	122.222	0.272	122.737	0.788	122.704	0.483	−0.033
	Q5	122.451	122.200	−0.250	122.514	0.063	122.504	0.304	−0.009
	DTQ	122.033	122.634	0.600	122.722	0.688	125.951	3.318	3.229
	DTQ5	122.006	122.053	0.046	123.618	1.612	123.617	1.565	−0.001
	Expt. [a]						119.1		
PN	D	113.260	116.954	3.695	114.561	1.301	117.872	0.918	3.311
	T	130.961	132.771	1.809	133.444	2.483	133.839	1.068	0.394
	Q	138.271	139.220	0.949	140.236	1.965	140.253	1.033	0.017
	5	141.416	141.634	0.219	142.619	1.203	142.621	0.986	0.002
	CBS limit								
	DT	138.415	139.430	1.015	141.395	2.981	140.561	1.132	−0.834
	TQ	143.605	143.926	0.321	145.192	1.587	144.934	1.008	−0.258
	Q5	144.715	144.168	−0.548	145.119	0.404	145.105	0.937	−0.014
	DTQ	143.414	143.660	0.246	144.051	0.638	144.559	0.900	0.508
	DTQ5	143.598	143.357	−0.241	143.978	0.380	144.273	0.915	0.294
	Expt. [a]						146.7		
Si_2	D	60.211	61.424	1.213	60.984	0.774	62.078	0.654	1.093
	T	69.536	70.205	0.668	70.355	0.819	70.455	0.250	0.100
	Q	72.815	73.224	0.409	73.558	0.743	73.554	0.330	−0.004
	5	74.154	74.277	0.122	74.533	0.379	74.540	0.263	0.006
	CBS limit								
	DT	73.463	73.902	0.439	74.300	0.838	73.982	0.080	−0.319
	TQ	75.208	75.427	0.219	75.896	0.688	75.816	0.389	−0.080
	Q5	75.559	75.381	−0.178	75.557	−0.002	75.574	0.193	0.017
	DTQ	74.593	74.806	0.212	75.221	0.628	75.374	0.568	0.152
	DTQ5	74.819	74.823	0.004	76.565	1.746	76.657	1.833	0.091
	Expt. [a]						74.9		

Frozen–core calculations utilized the cc-pVnZ and cc-pV(n+d)Z basis sets, while all-electron calculations utilized the cc-pCVnZ and cc-pCV(n+d)Z basis sets. $\Delta D_0(+d)$, represents the difference between D_0 for the augmented-d basis set and D_0 for the standard basis set. ΔE_{CV} is the difference between the valence and core–valence correlated calculations

[a] From [82] corrected for atomic spin-orbit splitting

[b] Values for SO_2 with cc-pVnZ and cc-pV(n+d)Z were obtained from [20]

[c] From [87] corrected for atomic spin-orbit splitting

calculation, this suggested a deficiency in the 2d set for cc-pCVDZ.

As shown in Table 3, the modified core–valence sets, cc-pCV(n+d)Z, resulted in a larger D_0 than the valence, sets, cc-pV(n+d)Z. This remedied the noted problem at the double-ζ level, where the all-electron cc-pCVnZ D_0 was actually smaller than cc-pV(n+d)Z D_0. $\Delta D_0(+d)$ was similar for the valence and for the core–valence basis sets. This suggested that the revised core–valence sets provide the improvement in the description of both atoms and molecules; this improvement is illustrated in Fig. 3 for sulfur and argon, and Fig. 4 for S_2 and SO_2. The greatest impact of the cc-pCV(n+d)Z basis sets occurred for the double-ζ level basis sets, and decreased as the basis set size was increased. The core–valence $\Delta D_0(+d)$ decreased more rapidly than the valence $\Delta D_0(+d)$ with respect to increasing basis set size, which resulted from the greater saturation of the orbital space when using the all-electron basis sets. The molecules that experienced the most significant improvements in energetic description were those containing both sulfur and oxygen. For example, for cc-pCV(D+d)Z, the D_0 of SO, SO_2, SO_3 were improved by 3.557, 13.201, 21.427 kcal/mol, respectively, over the D_0 determined using the cc-pCVDZ basis sets. All of the $\Delta D_0(+d)$ determined for PN were similar to those for SO, while the smallest impact was noted for Si_2 (e.g., 1.093 kcal/mol at the double-ζ level).

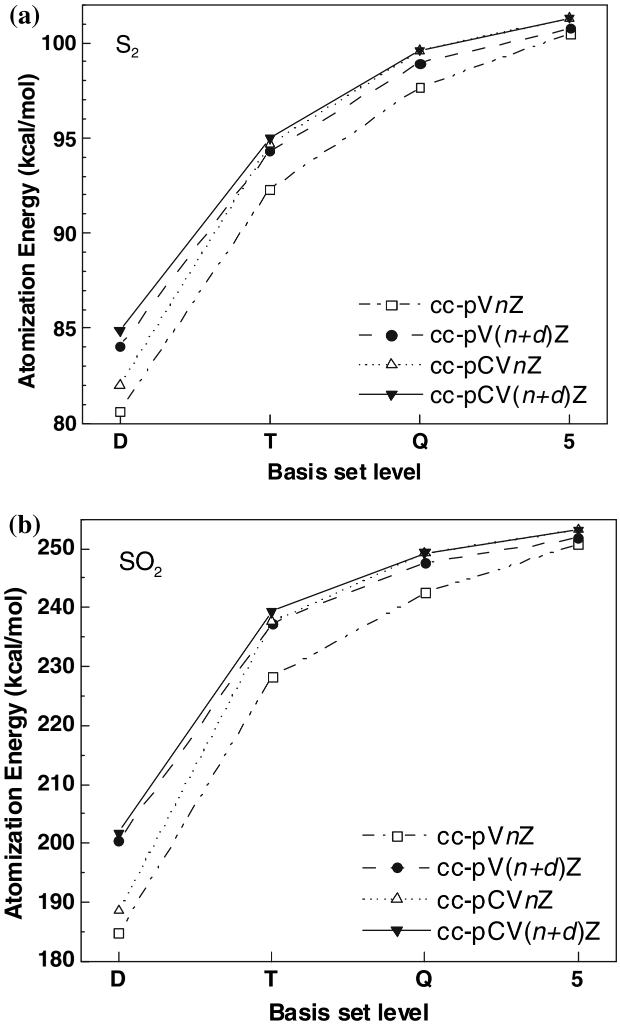

Fig. 4 Comparison of the atomization energy from valence-only calculations with cc-pV*n*Z and cc-pV(*n*+*d*)Z basis sets and from all-electron calculation with cc-pCV*n*Z and cc-pCV(*n*+*d*)Z basis sets for both the **a** S_2 and **b** SO_2

Table 4 Computed D_e (in kcal/mol) for CO, CO_2, NO, and NO_2 using CCSD(T)

Molecule	*n* =	cc-pV*n*Z	cc-pCV*n*Z	ΔE_{CV}
CO	D	241.486	242.490	1.004
	T	251.846	253.030	1.184
	Q	256.249	257.040	0.791
	5	257.548	258.330	0.782
CO_2	D	356.598	358.205	1.607
	T	376.063	378.134	2.072
	Q	383.894	385.673	1.779
	5	386.273	388.080	1.807
NO	D	131.843	132.522	0.679
	T	143.522	144.343	0.821
	Q	148.449	148.995	0.546
	5	150.185	150.682	0.497
NO_2	D	162.392	163.351	0.958
	T	182.325	183.251	0.925
	Q	190.280	190.753	0.473
	5	193.164	193.527	0.363

Frozen–core calculations utilized the cc-pV*n*Z, while all-electron calculations utilized the cc-pCV*n*Z basis sets. ΔE_{CV} is the difference between the valence and core–valence correlated calculations

Figure 4 depicts the D_0 values for S_2 and SO_2. The impact that the augmented-*d* basis sets made on D_0 is shown for both the valence-only and all-electron calculations. In comparing D_0 from the cc-pV*n*Z and cc-pCV *n*Z basis sets in Fig. 4, there is only a small increase in D_0 at the double-ζ level, whereas at the triple-ζ level, there is a much larger increase of the D_0. For the augmented-*d* sets, a more consistent improvement in D_0 is observed for the comparison of cc-pV(*n*+*d*)Z to cc-pCV(*n*+*d*)Z at each basis set level. However, the increase in D_0 arising from the use of the core–valence sets for the augmented-*d* sets is much smaller than that for the standard basis sets. This is due to the significant effect of the single tight-*d* function in the cc-pV(*n*+*d*)Z basis sets.

To account for core–valence effects in an additive type approach, ΔE_{CV} must be a reliable estimate of the core–valence energy, and as mentioned earlier, it is also important that ΔE_{CV} does not vary significantly with respect to basis set size. A common additive approach is to determine the core–valence effects at the triple-ζ level, as the double-ζ level may not provide a reasonable estimation of the core–valence correlation. As shown in Tables 3 and 5, computing ΔE_{CV} from an frozen–core cc-pV(D+*d*)Z and an all-electron cc-pCVDZ computation indeed would be unreliable and provide a core–valence correction of the wrong sign. In fact, this incorrect description of core–valence effects even arises at the triple-ζ level for SF_6, as shown in Table 6. Furthermore, ΔE_{CV} as shown in Table 3 for the cc-pCV*n*Z sets does not provide a consistent correction to the frozen–core calculation at any of the ζ-levels. For example, ΔE_{CV} for SO_3 changes by ~9 kcal/mol from the cc-pCVDZ to cc-pCVTZ level. This large jump in ΔE_{CV} was not seen in the small test set (CO, CO_2, NO, NO_2) of first-row molecules as shown in Table 4. The largest change in ΔE_{CV} from subsequent basis set levels was 0.464 kcal/mol from the double-ζ (1.607 kcal/mol) and triple-ζ (2.072 kcal/mol) of CO_2, which is much smaller than the 5.621 kcal/mol change found for SO_2 from the double-ζ (3.796 kcal/mol) and triple-ζ (9.417 kcal/mol). Interestingly, when the cc-pCV(*n*+*d*)Z sets are used for SO_2, there is only a 0.648 kcal/mol change in the ΔE_{CV} from double-ζ (1.319 kcal/mol) and triple-ζ (1.967 kcal/mol). Furthermore, the average change in ΔE_{CV} from subsequent basis sets in Table 4 is less than 0.1 kcal/mol when using the cc-pCV(*n*+*d*)Z sets. Overall, using the cc-pCV(*n*+*d*)Z basis

Table 5 Computed D_0 (in kcal/mol) for SO, SO_2, S_2, and PN using CCSD(T) and cc-pwCVnZ basis sets

Molecule	$n =$	cc-pwCVnZ	ΔE_{CV}
SO	D	99.037	4.339
	T	116.753	3.882
	Q	121.066	2.304
	5	122.928	0.973
SO_2	D	199.939	15.235
	T	240.794	12.504
	Q	249.720	7.195
	5	253.371	2.577
S_2	D	84.405	3.744
	T	95.260	2.957
	Q	99.755	2.085
	5	101.406	0.912
PN	D	117.169	3.909
	T	134.545	3.584
	Q	140.513	2.243
	5	142.737	1.322

ΔE_{CV} is the difference between the valence (from Table 3) and *weighted* core–valence correlated calculations

sets to estimate ΔE_{CV} for second-row systems provides a much more consistent core–valence correction, and the usefulness of this correction has already been demonstrated in the latest ccCA model chemistry benchmark studies [74,81].

A comparison of the performance of the cc-pCV(n+d)Z basis sets with that of the *weighted* core–valence basis sets, cc-pwCVnZ, for several molecules (SO, SO_2, S_2, and PN) has been made, as shown in Table 5. Overall, the performance of the cc-pwCVnZ sets for computing D_0 is similar to that of the cc-pC(V+d)Z sets; however, at the double-zeta level, the performance of cc-pwCVnZ is more alike to that resulting from frozen core, cc-pV(D+d)Z calculations for the description of the dissociation energy. The comparable performances of the cc-pwCVDZ and cc-pV(D+d)Z sets can be attributed to the similarities in d-functions present in both the cc-pwCVDZ and cc-pV(D+d)Z sets. However, the frozen-core cc-pV(D+d)Z D_0 for SO_2 is closer to experiment than the all-electron cc-pwCVDZ D_0. While this is not the case for all four molecules, this is an undesirable feature, which is caused by an unequal description of the core and valance regions. As explained earlier, cc-pV(D+d)Z basis sets are the recommended sets for valence correlation calculations; therefore core–valence basis sets should have additional core-d functions to provide a balanced description of both the core and valence regions, while currently both cc-pV(D+d)Z and cc-pwCVDZ have the identical number of d-functions.

As shown in Table 5, computing an approximate core–valence energy (ΔE_{CV}) for use as an additive correction, by taking the difference in the cc-pVnZ values in Table 3, produces exaggerated core–valence effects at the lower basis set levels; for example, ΔE_{CV} of SO_2 would be 12.504 kcal/mol at the cc-pwCVTZ level. Instead, if ΔE_{CV} was estimated as the difference in cc-pV(n+d)Z values in Table 3 and the cc-pwCVnZ values in Table 5, ΔE_{CV} would be nearer to the cc-pCV(n+d)Z ΔE_{CV} values, which for SO_2 would be 1.319, 1.967, 1.711, 1.404 kcal/mol when n = D, T, Q, 5, respectively. However, since there is an imbalance in the number of core-d and valance-d functions in these two basis sets, ΔE_{CV} becomes irregular when changing basis sets sizes; for example, the values of ΔE_{CV} for SO_2 are −0.444, 3.447, 2.115 and 1.536 kcal/mol as the basis set size is increased for the cc-pwCVnZ basis set series.

Additional computations have been performed on a small set of larger sulfur containing molecules (H_2SO_4, CH_3SH, CH_3SCH_3, and SF_6) in order to examine the impact of the new sets on the description of core–valence effects. For this test suite the geometry was obtained with MP2/cc-pVnZ for the CCSD(T)/cc-pCVnZ energy computation and MP2/cc-pV(n+d)Z for CCSD(T)/cc-pCV(n+d)Z where n = D and T. From Table 6, it is apparent that when more first-row atoms are bonded to sulfur $\Delta D_e(+d)$ becomes rather large. Even at the triple-ζ level, the $\Delta D_e(+d)$ can be quite substantial as shown for H_2SO_4 and SF_6 at 3.082 and 2.207 kcal/mol respectively. When using the cc-pCV(n+d)Z sets, ΔE_{CV} only varies by a few tenths of a kcal/mol from double-ζ to triple-ζ. This is not the case for the change in cc-pVnZ and cc-pCVnZ, which is inconsistent from double-ζ to triple-ζ,and can vary by ∼9 kcal/mol as shown for H_2SO_4 or as little as ∼0.5 kcal/mol in CH_3SH. It is not advisable to use the lower level cc-pCVnZ basis sets for this type of additive correction (ΔE_{CV}). However, as shown in Table 4, using the cc-pCV(n+d)Z sets allows for a consistent improvement over the cc-pV(n+d)Z sets at the different basis set levels. For example, ΔE_{CV} for H_2SO_4 is 2.734 and 3.304 kcal/mol with cc-pCV(D+d)Z to cc-pCV(T+d)Z, respectively, a change of only 0.57 kcal/mol, which is much smaller than the ∼9 kcal/mol shift ΔE_{CV} in seen with the cc-pCVnZ sets. Therefore, utilizing the cc-pCV(n+d)Z basis sets does allow for a reliable way to compute ΔE_{CV} for an additive correction, even at the cc-pCV(D+d)Z level.

4 Conclusions

The cc-pCVnZ basis sets for second-row atoms were revisited in order to design core–valence correlation consistent basis sets that build upon the recommended valence basis sets, cc-pV(n+d)Z. These revised core–valence basis sets provide a systematic description of the core–valence contribution to the total energy for all-electron calculations, and improve upon the description obtained using the cc-pCVnZ

Table 6 Computed D_e (in kcal/mol) for H_2SO_4, CH_3SH, CH_3SCH_3, and SF_6 using CCSD(T). Geometries were taken from the MP2/cc-pV*n*Z computations

Molecule	$n =$	cc-pVnZ	cc-pV$(n+d)$Z	$\Delta D_e(+d)$	cc-pCVnZ	ΔE_{CV}	cc-pCV$(n+d)$Z	ΔE_{CV}	$\Delta D_e(+d)$
H_2SO_4	D	467.186	495.076	27.890	474.628	7.442	497.810	2.734	23.183
	T	553.959	569.917	15.957	570.138	16.179	573.220	3.304	3.082
CH_3SH	D	437.592	439.675	2.083	439.493	1.902	441.223	1.548	1.729
	T	461.893	462.992	1.099	464.265	2.372	464.372	1.380	0.108
CH_3SCH_3	D	710.669	712.862	2.193	713.569	2.901	715.385	2.523	1.816
	T	748.909	750.080	1.171	752.349	3.440	752.458	2.378	0.109
SF_6	D	356.474	379.177	22.703	364.044	7.571	381.588	2.411	17.543
	T	440.141	454.281	14.139	453.838	13.697	456.045	1.764	2.207

Frozen–core calculations utilized the cc-pVnZ and cc-pV$(n+d)$Z basis sets, while all-electron calculations utilized the cc-pCVnZ and cc-pCV$(n+d)$Z basis sets. $\Delta D_e(+d)$, represents the difference between D_e for the augmented-*d* basis set and D_e for the standard basis set. ΔE_{CV} is the difference between the valence and core–valence correlated calculations

basis sets. As well, these revised sets remedy a problem noted in the calculation of dissociation energies for a series of molecules, where frozen-core calculations using the cc-pV(D+*d*)Z basis set yielded much larger dissociation energy than all-electron calculations using the cc-pCVDZ basis set. These revised sets are recommended for use in all-electron calculations involving second-row atoms (Al–Ar). The cc-pCV$(n+d)$Z sets provide a reliable and consistent means to evaluate ΔE_{CV} for use as an additive core–valence correction to a frozen–core calculation, even at the double-ζ level, which is not possible with the original basis sets due to the inconsistency in the core–valence values (defined by Eq. 1) with respect to increasing basis set size.

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