

## Revisiting the Atomic Natural Orbital Approach for Basis Sets: Robust Systematic Basis Sets for Explicitly Correlated and Conventional Correlated *ab initio* Methods?

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**Abstract:** The performance of several families of basis sets for correlated wave function calculations on molecules is studied. The widely used correlation-consistent basis set family cc-pVXZ ( $n = D, T, Q, 5$ ) is compared to a systematic series of atomic natural orbital basis sets (ano-pVXZ). These basis sets are built from the cc-pV6Z primitives in atomic multireference average coupled pair functional (MR-ACPF) calculations. Segmented basis sets optimized for self-consistent field calculations (def2-SVP, def2-TZVPP, and def2-QZVPP as well as “pc- $n$ ”,  $n = 1, 2, 3$ ) were also tested. Reference Hartree–Fock energies are determined with the uncontracted aug-cc-pV6Z basis set for a set of 21 small molecules built from H, B, C, N, O, and F. Reference coupled cluster CCSD(T) correlation energies were determined from extrapolation at the cc-pV5Z/cc-pV6Z level. It is found that the ano-pVXZ basis sets outperform the other basis sets. The error in the SCF energies compared to cc-pVXZ basis sets is reduced by about a factor of 3 at each cardinal number. In addition, the ano-pVXZ consistently recovers more correlation energy than their competitors at each cardinal number. The ability of the four families of basis sets to extrapolate SCF and correlation energies to the basis set limit has been investigated. A conclusion by Truhlar is confirmed that the optimum exponent for correlation energy extrapolations at the DZ/TZ level is  $\sim 2.4$ . All TZ/QZ basis set pairs lead to an optimum exponent close to the expected value of 3. The SCF energy extrapolation proposed by Petersson and co-workers is found to be effective. At the DZ/TZ level, errors in *total* energies of less than 2 mEh are found for the test set, while at the TZ/QZ level one obtains the total energies within  $\sim 0.3$  mEh of the basis set limit. For extrapolation, the “cc” and “ano” bases are found to be similarly successful. Extrapolation results were compared to explicitly correlated calculations with dedicated basis sets (cc-pVXZ-F12) as well as the ano-pVXZ bases. It is found that the ano-pVXZ+ basis sets perform as well as the cc-pVXZ-F12 family (both are of comparable size); additional improvement should be possible by reoptimizing the ANO basis sets for explicitly correlated calculations. The error of the extrapolated energies is about 2–3 times smaller than what was found in the explicitly correlated calculations. However, the error in the explicitly correlated calculations is more systematic, and hence the same conclusion may not hold for the computation of energy differences.

### 1. Introduction

It is well-known that the one-particle basis set is an important ingredient of wave-function-based *ab initio* calculations on molecules. While the convergence of the Hartree–Fock

energy to the basis set limit is relatively rapid as the one-particle basis set is approaching completeness, the convergence of the correlation energy is known to be slow.<sup>1</sup> In order to obtain accurate results for energetic quantities, very large basis sets of at least polarized quadruple- $\zeta$  quality or even larger are required. Such basis sets quickly become

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unmanageably large even for relatively small molecules (say, beyond five non-hydrogen atoms).

In recent years, two techniques have emerged that aim at obtaining accurate results for correlated *ab initio* energies with smaller basis sets. The first family of methods corrects the origin of the slow basis set convergence of the correlation energy—the lack of derivative discontinuity (cusp) in standard wave functions when electrons meet each other. The *explicitly correlated* methods accomplish this by introducing the interelectronic distances  $r_{ij}$  explicitly into the wave function *ansatz*; this can be viewed alternatively as an inclusion of  $r_{ij}$ -dependent many-electron basis functions. The most practical of these methods were pioneered by Kutzelnigg;<sup>2</sup> the *R12 methods* developed by him and many others allow for approaching the basis set limit with much smaller basis sets. Great progress has been made in recent years in the formulation and implementation of explicitly correlated wave function methods. An authoritative review of these approaches is provided in a recent article by Helgaker et al.<sup>3</sup>

The second family of methods relies on extrapolation of the correlation energy based on a series of calculations with successively refined basis sets.<sup>4,5</sup> There are two key requirements for this approach: (a) the existence of a systematically converging series of basis sets and (b) a suitable formula for correlation energy extrapolation.

Dunning and co-workers made a major contribution by developing a series of successively larger one-particle basis sets, cc-pVXZ with  $n = 2$  (= D), 3 (= T), 4 (= Q), 5, 6, etc. being the “cardinal number”; cc stands for “correlation consistent” and p for “polarized”.<sup>6–15</sup> Using these basis sets, the calculated correlation energies (within a given correlation method) converge smoothly and systematically to the basis set limit. The cc-basis sets are built upon a core of Hartree–Fock orbitals and are systematically supplemented with additional primitive Gaussian functions that describe polarization and valence shell correlation. For  $n = 2, 3, 4$ , etc., the polarization sets for main group elements consist of 1d, 2d1f, 3d2f1g, etc. functions. For the hydrogen and helium atoms, the equivalent sets consist of 1p, 2p1d, 3p2d1f, etc. functions. Further modifications include additional diffuse functions for weak interactions and calculations on anions (aug-cc-pVXZ)<sup>10</sup> and functions that describe core-correlation (cc-pCVXZ<sup>9,16</sup>) or core–valence correlation (cc-pwCVXZ<sup>6,9</sup>). Recently, Peterson and co-workers have developed correlation consistent basis sets for first through third row transition metals.<sup>17–20</sup> Reconstructions of the basis sets to comply with scalar relativistic Douglas–Kroll–Hess (DKH) calculations are also available.

A second way to construct systematic series of one-particle basis sets was pioneered by Almlöf and Taylor and is based on atomic natural orbitals (ANOs).<sup>18–22</sup> ANO basis sets are generally contracted in the sense that all Gaussian primitives of a given angular momentum contribute to all basis functions. ANOs are among the best possible choices for atomic correlation calculations. It is, however, not a priori clear whether ANOs are flexible enough to properly describe low symmetry molecular environments and the changes of the atomic orbitals upon bond formation and charge transfer. Many excellent results have, however, been obtained with

the use of ANOs, and they are the main workhorse of the MOLCAS quantum chemistry program.<sup>21–23</sup> The *general contraction* scheme on ANOs poses new challenges on the integral evaluation program: the two-electron integral evaluation time naively depends on the fourth power of the contraction depth, although the scaling is reduced to quadratic by using the robust density fitting (aka resolution of the identity, RI) approach.<sup>24</sup> Only a few modern quantum chemistry programs can efficiently handle generally contracted basis sets.

In SCF calculations, the computing time is strongly dominated by the integral evaluation time, and hence one seeks to develop basis sets with the smallest possible number of primitives. This has been the route followed by Ahlrichs and co-workers in the development of the def- series of basis sets that is available in double- $\zeta$  (def2-SVP), triple- $\zeta$  (def2-TZVPP), and quadruple- $\zeta$  (def2-QZVPP) variants.<sup>28–32</sup> For these basis sets, exponents and contraction coefficients are optimized in atomic calculations. The def2 bases usually show excellent performance in Hartree–Fock and DFT studies. The behavior of these basis sets in MP2 calculations has been studied by their developers,<sup>25,26</sup> but the behavior in highly correlated calculations has probably not been fully assessed to date.

A similar target has been followed with the development of the pc- $n$  ( $n = 0, 1, 2, 3, 4$ ) basis sets by Jensen and co-workers.<sup>27–33</sup> The basis sets of double- through quintuple- $\zeta$  quality were designed to systematically converge to the SCF basis set limit. These basis sets are partially optimized in molecular calculations.

The motivation for the present study was the efficient application of *accurate* correlation methods for large molecules. Since the overall cost is dominated by the calculation of the correlation energy for which the integral evaluation time is less of an issue, the most important aspect is the number of basis functions with which a given accuracy can be obtained. Clearly, the error relative to the basis set limit contains contributions from the SCF error and the correlation energy error. Hence, one desires basis sets that, for a given size, perform well in both respects. In this context, we became somewhat unsatisfied with the correlation-consistent basis sets that provide excellent correlation energies but also show errors in the Hartree–Fock energies that are significantly larger than what is obtained with other basis sets of the same size. We were curious of whether one could improve on this behavior while maintaining good correlation energies. This is also relevant in the context of explicitly correlated calculations where one aims at accurate correlation energies with small basis sets. The present work represents an attempt to systematically evaluate the performance of series of basis sets for which at least double-, triple-, and quadruple- $\zeta$  variants are available. Particularly important are the double- and triple- $\zeta$  members within each series since calculations with larger basis sets are hardly feasible in “real life” chemical applications. Since errors can be largely reduced through extrapolation and R12 techniques, we have also evaluated the performance of the various basis sets with respect to SCF and correlation energy extrapolations using these two approaches.

## 2. Basis Set Construction

A series of ANO basis sets was constructed in the course of this study. It is obvious that no basis set can be more accurate than the underlying set of primitives. Hence, we have used the primitives of the cc-pV6Z basis set<sup>34</sup> as a starting point. In order to keep the calculations manageable, a two-step procedure was pursued.

The ANO basis sets were obtained from calculations on the neutral atoms. To this end, the cc-pV6Z basis set was fully decontracted. Atomic CASSCF calculations were carried out for the atomic ground terms. The atomic calculations were tightly converged on the atomic ground terms while carefully averaging over the spatially degenerate member of the terms. For example, for the <sup>3</sup>P state of the carbon atom, all three triplet roots corresponding to the three components of the P-state were determined. Multireference averaged coupled pair functional (MR-ACPF<sup>15</sup>) calculations were performed on top of the CASSCF ground states. The MR-ACPF method has the advantage over MR configuration interaction (MR-CI) of being (nearly) size consistent and leading to a stationary solution with a well-defined density.<sup>35</sup> For the MR-ACPF calculations, all configurations in the CAS space were kept as references, even those of the “wrong” symmetry and insufficient number of open-shell orbitals. The first-order interacting space is left uncontracted, and no selection or any other approximation was made. The densities of all three components of the P states were averaged in order to obtain a spherically symmetric density that was subsequently diagonalized in order to obtain atomic natural orbitals. All valence electrons were correlated. Thus, the cores of our ANO basis sets are orbitals optimized at the CASSCF level.

Three families of basis sets were constructed in order to investigate the transition from cc-basis sets to ANO basis sets:

(1) acc-pVXZ: The original polarization functions of the cc-pVXZ basis were kept, and only the s and p functions were replaced by their ANO counterparts. The number of primitives is 16 for the s functions and 12 for the p functions (B–Ne).

(2) rcc-pVXZ: the same s and p contractions as in cc-pVXZ were used, but the polarization functions were replaced by ANO contractions. The same numbers of contracted polarization functions were kept as in the cc-pVXZ family, e.g., 1d for  $n = 2$ , 2d1f for  $n = 3$ , and 3d2f1g for  $n = 4$ . The number of primitives is five for the d contractions, four for the f contractions, and three for the g contractions.

(3) ano-pVXZ: All orbitals were left at their complete ANO contractions as described above. For hydrogen, the appropriate number of ANOs is taken from the original NASA-AMES ANO set.<sup>35,36</sup>

The hydrogen basis for the ano-pVXZ and acc-pVXZ basis sets was taken from the original NASA-AMES-ANO basis,<sup>37</sup> while in keeping with the philosophy of the basis set construction, the s and p part for the rcc bases came from the original cc-bases and the polarization functions from the NASA-AMES set.

Thus, by construction the four families of basis sets cc-pVXZ, acc-pVXZ, rcc-pVXZ, and ano-pVXZ all have the same number of basis functions for a given  $n$  but differ in their contraction depth.

For comparison, the segmented basis sets def2-SVP, def2-TZVPP, and def2-QZVPP developed by Ahlrichs and co-workers as well as the polarization consistent basis sets of Jensen (pc- $n$ ,  $n = 1, 2, 3$ ) were included in the study. Furthermore, alternative ANO sets due to Roos and co-workers<sup>23,36</sup> as well as the original, pioneering quadruple- $\xi$  type ANO basis by Almlöf and Taylor<sup>24</sup> were included in the study. The number of basis functions is comparable or even identical to the other basis sets included in the study, and hence a comparison is appropriate.

## 3. Calculations

Twenty-seven basis sets have been evaluated by performing molecular calculations. In order to judge the performance of the basis sets, the Hartree–Fock energy as well as the correlation energy at the CCSD(T) level will be employed. The SCF energies calculated with the very large uncontracted aug-cc-pV6Z basis set serve as a near HF limit reference. We expect the deviation of the reference values from the true Hartree–Fock limit to be below 0.1 mEh. Reference values for the correlation energies were obtained by using the standard two-point extrapolation scheme involving the cc-pV5Z and cc-pV6Z basis sets, as will be detailed below.

As test systems, the hydrides H<sub>2</sub>, BH<sub>3</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and FH were chosen together with all possible diatomics built from B, C, N, O, and F. Open-shell species were treated in the spin-unrestricted formalism. A reviewer pointed out that we have inadvertently used an excited state of BN. For the purposes of this paper, this choice is immaterial. The geometries were taken from geometry optimizations at the B3LYP/def2-TZVP level. Geometric parameters are given in the Computational Details section.

## 4. Comparison of Basis Sets

The reference values used in the present study are collected in Table 1. The results of the test calculations are summarized in terms of statistical measures in Table 2. Individual results for all molecules and basis sets are given in the Supporting Information.

**4.1. SCF Energies.** The performance of the various double- $\xi$  basis sets varies fairly dramatically. The largest absolute errors are obtained with the def2-SVP basis set that has been designed with the smallest possible number of primitive Gaussians in mind. Hence, calculations with def2-SVP are very efficient, and many successful molecular studies have been performed with this basis set. Nevertheless, it is the one with the largest deviations from the Hartree–Fock limit in the present study. Perhaps surprisingly, the second largest errors are obtained from the pc-2 basis set that has also been designed for SCF (Hartree–Fock and DFT calculations). Third in line is the cc-pVDZ basis set that shows a mean unsigned deviation from the basis set limit of about 40 mEh in the present test set.

**Table 1.** Reference SCF and Correlation Energies for the Present Study

molecule	SCF-reference	EC(CCSD(T)) cc-pV5Z	EC(CCSD(T)) cc-pV6Z	E(CCSD(T)) cc-pV(5/6)Z	Etot(CCSD(T))
H <sub>2</sub> ( <sup>1</sup> Σ)	-1.133583	-0.04065	-0.04076	-0.04090	-1.17449
BH <sub>3</sub> ( <sup>1</sup> A)	-26.402596	-0.14446	-0.14505	-0.14586	-26.54846
CH <sub>4</sub> ( <sup>1</sup> A)	-40.216965	-0.23767	-0.23884	-0.24044	-40.45741
NH <sub>3</sub> ( <sup>1</sup> A)	-56.224824	-0.27479	-0.27660	-0.27909	-56.50392
H <sub>2</sub> O ( <sup>1</sup> A)	-76.066958	-0.30233	-0.30499	-0.30866	-76.37561
HF ( <sup>1</sup> A)	-100.070300	-0.31511	-0.31874	-0.32372	-100.39402
B <sub>2</sub> ( <sup>3</sup> Σ)	-49.086197	-0.17822	-0.17885	-0.17972	-49.26592
BC ( <sup>4</sup> Σ)	-62.337076	-0.19774	-0.19887	-0.19970	-62.53678
BN ( <sup>3</sup> Σ)	-79.021852	-0.27087	-0.27280	-0.27547	-79.29732
BO ( <sup>2</sup> Σ)	-99.566250	-0.34236	-0.34539	-0.34955	-99.91580
BF ( <sup>1</sup> Σ)	-124.168631	-0.38238	-0.38632	-0.39172	-124.56035
C <sub>2</sub> ( <sup>1</sup> Σ)	-75.406555	-0.39968	-0.401452347	-0.40275	-75.80930
CN ( <sup>2</sup> Σ)	-92.234733	-0.35337	-0.35581	-0.35916	-92.59389
CO ( <sup>1</sup> Σ)	-112.791245	-0.40711	-0.41052	-0.41521	-113.20646
CF ( <sup>2</sup> Π)	-137.238721	-0.41972	-0.42407	-0.43004	-137.66876
N <sub>2</sub> ( <sup>1</sup> Σ)	-108.994314	-0.42002	-0.42329	-0.42778	-109.42209
NO ( <sup>2</sup> Π)	-129.309819	-0.45716	-0.46120	-0.46675	-129.77657
NF ( <sup>3</sup> Σ)	-153.852696	-0.45705	-0.46194	-0.46867	-154.32136
O <sub>2</sub> ( <sup>3</sup> Σ)	-149.691600	-0.49790	-0.50271	-0.50931	-150.20090
OF ( <sup>2</sup> Π)	-174.210823	-0.53157	-0.53748	-0.54560	-174.75642
F <sub>2</sub> ( <sup>1</sup> Σ)	-198.775205	-0.60622	-0.61330	-0.62302	-199.39823

It is interesting how much better one can get with an ANO basis set. In fact, the error with the ano-pVDZ basis is more than a factor of 3 smaller than what is achieved with cc-pVDZ and an order of magnitude smaller than the error obtained with the def2-SVP basis. This accuracy is obtained despite the fact that both basis sets contain the same number of contracted basis functions. The comparison of the ano-pVDZ, acc-pVDZ, rcc-pVDZ, and cc-pVDZ basis sets reveals that the improvement in the SCF energy is mainly due to the highly contracted ANO s and p parts of the basis set and to a lesser extent to the contracted single polarization function.

Already at the triple- $\zeta$  level with 2d1d and 2p1d polarization sets, a more uniform performance of the various basis sets is obtained. The basis set that leads to the highest energies is the cc-pVTZ one, closely followed by pc-2. The performance of the def2-TZVPP basis set is excellent, and it only gives a mean unsigned error of about 5 mEh. However, once more, the improvement obtained with the ano-pVTZ basis set is highly significant. The error is again more than a factor of 3 smaller than that obtained with the cc-pVTZ basis and only amounts to about 2.5 mEh on average. This is almost as good as the result obtained with the much larger cc-pVQZ basis.

For the quadruple- $\zeta$  bases, all basis sets provide results within 2.5 mEh from the reference values. Once more, the by far largest error is obtained with cc-pVQZ, followed by acc-pVQZ, which has the same s and p functions. The best results are obtained with def2-QZVPP, which comes within 0.6 mEh of the reference values. In this respect, it is marginally better than the ano-pVQZ basis set that shows an error that is 0.2 millihartree larger. However, def2-QZVPP is also slightly larger in terms of basis functions than cc-pVQZ or ano-pVQZ. The same is true for pc-3, which contains an extra set of s and p functions for B–Ne but is still slightly less accurate than ano-pVQZ.

It is instructive to observe that very significant improvements in the results can be obtained by merely adding an additional set of s and p functions to the basis set without

extending the polarization set. This leads to sano-pVDZ+ (s stands for small in this case). For the sano-pVDZ+ basis set, the mean unsigned error in the SCF energy is only 7.0 mEh, which is almost half of the error obtained with ano-pVDZ and already better than what is obtained with the much larger cc-pVTZ or pc-2 bases. In fact, for the sano-pVTZ+ basis set where the four additional basis functions are even less problematic, the mean unsigned error drops to 1.4 mEh, which is about half of what one gets from the much larger cc-pVQZ basis. Even for the sano-pVQZ+ basis, an improvement is obtained, and a mean unsigned error of only 0.5 mEh results. Since sano-pVQZ+ is about the same size as def2-QZVPP, this shows that ANO basis sets are even competitive in terms of accuracy with dedicated SCF optimized bases, even though they have never been designed for this purpose.

By adding the next d function to the polarization set and an extra s function, one obtains ano-pVDZ+ (5s3p2d for B–Ne), which improves the results further, and for ano-pVTZ+, the average unsigned error even drops below 1 mEh. In terms of ANOs, one can also think about the ano-pVXZ+ basis sets as being identical to the ano-pV(n+1)Z basis set with the highest angular momentum polarization function deleted and an extra s function added (the latter does not add significantly to the computational cost and mainly improves the SCF energies). Hence, these basis sets are significantly larger than the ano-pVXZ bases.

In a comparison of our results to the those of the ANO bases of Roos and co-workers and Almlöf and Taylor, we observe that the results are fairly similar, with slight advantages for the ano-pVXZ basis sets constructed in this work.

In summary, from the results collected in Table 2, one concludes that ANO basis sets yield excellent SCF energies. In fact, the results obtained with ano-pVXZ are almost as good as what one obtains from cc-pV(n+1)Z and also as good or even better than what one obtains with basis sets that are specifically optimized for SCF calculations. This behavior was not anticipated and is important in the context of explicitly correlated calculations, as will be discussed below.



**Table 2.** Errors (in mEh) in SCF and Correlation Energies Relative to the Uncontracted cc-pV6Z and Complete Basis Extrapolated Reference Values Respectively<sup>a</sup>

basis set	MUE(SCF)	MUE(EC)	% $\Delta E_C$	RMS(SCF)	RMS(EC)	MAX(SCF)	MAX(EC)	MUE( $E_{\text{tot}}$ )
cc-pVDZ	39.9	98.1	26.1	45.7	110.8	88.2	213.3	138.0
cc-pVTZ	9.8	35.5	9.2	11.1	40.8	21.3	81.0	45.3
cc-pVQZ	2.2	14.6	3.7	2.5	17.0	5.0	34.4	16.7
pc-1	74.4	100.9	27.2	84.2	113.7	158.8	222.6	175.2
pc-2	8.3	43.7	11.4	9.1	50.1	15.4	100.3	52.0
pc-3 <sup>b</sup>	0.9	<b>(13.3)</b>	<b>(3.4)</b>	0.9	15.5	<b>(1.3)</b>	31.5	14.2
def2-SVP	128.2	99.2	26.4	144.0	112.1	266.8	216.2	227.4
def2-TZVPP	4.9	36.9	9.6	5.4	42.4	9.0	84.1	41.8
def2-QZVPP <sup>c</sup>	<b>(0.6)</b>	15.6	4.0	<b>(0.7)</b>	18.2	<b>(1.2)</b>	36.8	16.2
ano-pVDZ	<b>13.1</b>	<b>82.6</b>	<b>21.9</b>	<b>15.0</b>	<b>92.9</b>	<b>29.0</b>	<b>173.0</b>	<b>95.7</b>
ano-pVTZ	<b>2.6</b>	<b>30.4</b>	<b>7.9</b>	<b>2.8</b>	<b>34.9</b>	<b>4.5</b>	<b>65.9</b>	<b>33.0</b>
ano-pVQZ	<b>0.8</b>	<b>12.9</b>	<b>3.3</b>	<b>0.9</b>	<b>15.0</b>	<b>1.7</b>	<b>28.4</b>	<b>13.7</b>
acc-pVDZ	16.6	92.5	24.5	18.3	104.7	30.2	202.2	109.2
acc-pVTZ	3.7	35.6	9.3	4.1	40.5	7.0	78.5	39.3
acc-pVQZ	1.1	15.2	3.9	1.2	17.6	2.3	35.6	16.2
rcc-pVDZ	36.3	89.1	23.7	42.0	100.5	83.1	192.9	125.5
rcc-pVTZ	9.0	32.1	8.3	10.4	36.8	20.3	72.4	41.1
rcc-pVQZ	2.0	13.4	3.4	2.4	15.5	4.8	31.3	15.4
larger default basis sets								
aug-cc-pVDZ	32.4	84.1	22.4	37.3	94.4	75.0	177.1	116.5
aug-cc-pVTZ	8.2	29.8	7.8	9.4	34.1	18.6	66.3	38.0
aug-cc-pVQZ	1.7	12.2	3.1	2.0	14.2	4.4	28.3	14.0
sano-pVDZ+	7.0	67.3	17.6	7.9	76.4	13.1	143.3	74.3
sano-pVTZ+	1.4	12.4	6.9	1.5	30.9	2.5	58.5	28.2
sano-pVQZ+	0.5	11.9	3.1	0.5	13.8	0.9	26.5	12.3
ano-pVDZ+	5.0	53.4	13.7	5.7	61.6	11.0	115.4	58.4
ano-pVTZ+	0.9	20.9	5.4	1.0	24.1	2.0	47.6	21.8
ano-pVQZ+	0.2	8.7	2.3	0.3	9.9	0.5	19.5	8.9
Roos-ANO-DZP <sup>d</sup>	6.7	65.8	17.6	7.7	73.4	15.7	133.5	72.5
Roos-ANO-TZP <sup>d</sup>	1.4	23.3	6.1	1.6	26.6	2.7	51.0	24.6
NASA-AMES-ANO <sup>e</sup>	1.1	12.4	3.2	1.2	14.3	1.6	28.3	13.4
explicitly correlated (R12) CCSD(T) <sup>e</sup>								
ano-pVDZ	<b>13.1</b>	22.1	6.5	<b>15.0</b>	25.4	<b>29.0</b>	51.7	23.1
ano-pVTZ	<b>2.6</b>	7.5	2.1	<b>2.8</b>	9.1	<b>4.5</b>	19.7	7.7
ano-pVQZ	<b>0.8</b>	2.8	0.8	<b>0.9</b>	3.4	<b>1.7</b>	7.6	2.8
ano-pVDZ+	5.0	11.5	3.3	5.7	13.3	11.0	26.9	11.8
ano-pVTZ+	0.9	3.6	1.0	1.0	4.4	2.0	9.5	3.6
ano-pVQZ+	0.2	1.6	0.5	0.3	1.9	0.5	4.0	1.6
cc-pVDZ	39.9	25.1	7.6	45.7	28.3	88.2	55.3	27.8
cc-pVTZ	9.8	9.0	2.5	11.1	10.9	21.3	23.5	9.5
cc-pVQZ	2.2	3.7	1.0	2.5	4.6	5.0	10.2	3.9
aug-cc-pVDZ	32.4	16.0	4.8	37.3	17.7	75.0	32.7	17.2
aug-cc-pVTZ	8.2	6.1	1.7	9.4	7.3	18.6	15.7	6.2
aug-cc-pVQZ	1.7	2.7	0.7	2.0	3.4	4.4	7.6	2.7
cc-pVDZ-F12	10.8	13.5	3.8	12.3	16.1	22.8	34.8	13.9
cc-pVTZ-F12	2.0	5.0	1.4	2.3	5.8	4.7	11.9	5.1
cc-pVQZ-F12	0.2	1.7	0.5	0.2	2.0	0.3	4.1	1.8

<sup>a</sup> The best result in each category of basis set (DZ, TZ, QZ) is printed in bold. If the best result is obtained with a slightly larger basis set, it is put in parentheses. MUE = mean unsigned error; RMS = root-mean square error; MAX = maximum error; SCF = Hartree-Fock energy; EC = CCSD(T) correlation energy. <sup>b</sup> The pc-3 basis set contains 6s5p4d2f1g contractions for B–Ne and is therefore the same size as sano-pVQZ+. <sup>c</sup> The def2-QZVPP basis set contains 7s4p3d2f1g contractions and is therefore of similar size to sano-pVQZ+. <sup>d</sup> The Roos-ANO basis sets contain the same number of functions as the ano-pVDZ+ and ano-pVTZ+ basis sets. NASA-AMES ANO is the same size as ano-pVQZ. <sup>e</sup> The CABS correction to the SCF energies have been included in the right-most column.

**4.2. Correlation Energies.** The main purpose of this study is to evaluate how the various basis sets perform in correlation energy calculations. As is evident from Table 2, the behavior of the basis sets is more uniform in this respect. With the DZ bases, one recovers 70–80% of the correlation energy; with TZ bases, about 90%; and with QZ bases, about 96–98%. However, there are still differences between the various construction schemes.

Again, the most accurate among the DZ bases is ano-pVDZ, which, on average, recovers about 4% or in absolute terms 20 mEh more correlation energy than the basis sets with uncontracted polarization functions. Here, the compari-

son with rcc-pVDZ and acc-pVDZ reveals that this is mainly due to the contracted polarization function and to a lesser extent to the more extensive s and p contractions. The differences among the other DZ bases are quite small.

A similar but much less pronounced result is obtained at the TZ level where ano-pVTZ is about 1–3% (or about 5 mEh on average) better than the other basis sets of the same size.

Interestingly, the differences almost vanish at the QZ level where there are only small differences between all QZ bases. All results are within 0.5% or 1–2 mEh of each other, and all deviate by 3–4% from the reference values.

It is obvious from the results obtained with sano-pVXZ+ and ano-pVXZ+ that limited improvements can be obtained from further augmentation of the basis set. The sano-pVDZ+ results are significantly better ( $\sim 4\%$ ) than those obtained with ano-pVDZ, but already sano-pVTZ+ is rather similar to ano-pVTZ. The comparison between ano-pVXZ+ and ano-pV( $n+1$ )Z confirms that in order to reach the next level of accuracy it is more important to add the next higher angular momentum polarization function rather than to extend the existing polarization sets.

**4.3. Total Energies.** Since the ano-pVXZ basis sets of a given size have shown the best SCF and simultaneously the best correlation energies, it is trivial that they also show the best total energy in comparison with the reference values. The effects are most pronounced for the DZ and TZ basis sets where the ANO-basis sets are clearly superior to the “def2”, “cc”, and “pc” bases of the same size. For the QZ bases, all construction schemes start to converge to the same values, and the mean unsigned deviations are all between 13 and 16 mEh for the present test set. This error is dominated by the errors in the correlation energies that are still an order of magnitude larger than the SCF error.

**4.4. Explicitly Correlated (R12) Energies.** We also performed a series of CCSD(T)<sub>R12</sub> calculations using the newly developed ano-pVXZ basis sets as well as standard correlation-consistent basis sets (cc-pVXZ and aug-cc-pVXZ) and the recently developed cc-pVXZ-F12 basis set of Peterson et al., who specifically optimized their basis sets for R12 methods.<sup>36</sup> The immediate objective of these efforts was to examine whether the newly developed ANO basis sets are suitable for R12 methods, even though they were not constructed with such calculations in mind. We also wanted to see whether it is worth employing the ANO approach for constructing basis sets specifically suited for explicitly correlated (R12) methods.

Because the R12 correction only reduces the basis set error of the correlation energy, the basis set error of the SCF energy is relatively more significant in the context of explicitly correlated methods. The RMS error of the (aug)-cc-pVXZ SCF energy is larger than that of the correlation energy for  $X = D$ , is comparable to the latter for  $X = T$ , and is smaller than the latter for  $X = Q$ . With the ano-pVXZ basis sets—by virtue of their much improved SCF energy—the correlation energy error is always greater than the error of SCF energy. Peterson et al. used this observation in the design of the cc-pVXZ-F12 basis sets: the cc-pVXZ-F12 basis is similar in structure to the aug-cc-pVXZ basis, with the exception of more  $s$  and  $p$  primitives and the greater number of  $s$  and  $p$  shells in the former. The latter feature is largely responsible for the improved SCF energies obtained with the VXZ-F12 basis sets. The additional  $s$  and  $p$  functions dramatically reduce the basis set error of the cc-pVXZ-F12 SCF energy compared to its (aug)-cc-pVXZ counterpart. As a result, the basis set error of SCF energy with cc-pVXZ-F12 bases is always much smaller than that of the corresponding CCSD(T)<sub>R12</sub> correlation energy. The ano-pVXZ basis sets are comparable in their SCF energy performance to the cc-pVXZ-F12 counterparts, except for  $X = Q$ . The

ano-pVXZ+ family, as expected, produces the smallest SCF energy errors.

Note that the error of SCF energy can be greatly reduced by including the CABS singles correction: indeed, the mean unsigned error of the total energy including the CABS correction is similar to the error of correlation energy with all basis sets. Although the evaluation of the CABS singles correction requires the evaluation of Coulomb integrals with two auxiliary basis set indices, its cost is negligible compared to that of the R12 correction. Without such a correction, the ano-pVXZ and cc-pVXZ-F12 basis sets produce smaller SCF energy errors and thus should be preferred to the cc-pVXZ and aug-cc-pVXZ series.

Let us now turn our attention to the basis set error of CCSD(T)<sub>R12</sub> correlation energy. The initial applications of modern R12 methods utilized the standard correlation-consistent basis set families. The cc-pVXZ series was, however, found to result in less accurate correlation energies than its aug-cc-pVXZ counterpart; thus all applications of R12 methods used the augmented correlation-consistent series. However, the aug-cc-pVXZ basis sets contain highly diffuse functions, and molecular studies in “real life” applications are often complicated by (near) linear dependencies in the basis set. For ANO basis sets, the higher members of a given angular momentum contain more and more nodes that extend into the outer region of the molecule, and hence these functions may take on the role of diffuse functions. However, the lack of uncontracted diffuse primitives in the ANO basis sets may lead to problems in the calculations of weak interactions and on anions or highly excited states. These subjects will be investigated in the future.

The performance of the newly developed ano-pVXZ series for R12 correlation energies falls in between the cc-pVXZ and aug-cc-pVXZ series: ano-pVDZ basis results in RMS correlation energy error similar to that of cc-pVDZ, whereas the ano-pVQZ basis is comparable in that sense to the aug-cc-pVQZ basis. The ano-pVXZ+ basis sets, which have the same number of functions as the aug-cc-pVXZ family, are significantly better than the latter. *These encouraging findings suggest that the uncontracted low-exponent (diffuse) basis functions do not have to be included in larger basis sets for R12 calculations*; as mentioned above, avoiding such functions is crucial for avoiding linear dependencies and poorly conditioned equations in computations on large molecules.

The ano-pVXZ basis sets are inferior to the cc-pVXZ-F12 basis sets for computing correlation energies with R12 methods. However, the ano-pVXZ+ basis sets, which have even slightly fewer basis functions than the cc-pVXZ-F12 basis sets, produce the most accurate correlation energies. For example, the RMS( $E_c$ ) obtained with the ano-aug-pVQZ basis is 1.9 millihartree, which is 0.1 millihartree smaller than that with the cc-pVQZ-F12 basis. This is an interesting finding: the cc-pVXZ-F12 series was designed specifically for R12 methods, whereas the new ano-pVXZ+ series was not. For example, the structure of cc-pVXZ-F12 bases is similar to that of aug-cc-pVXZ; the former yield smaller RMS( $E_c$ )’s due to the reoptimized polarization functions;

this suggests that reoptimization of the (aug)-ano-pVXZ basis sets for R12 methods may improve their performance similarly.

Thus, the limited set of explicitly correlated calculations with the new ano-pVXZ+ basis set series hints that specific optimization of ANO basis sets for R12 calculations might be fruitful. Potential improvement to the level of what is obtained with the cc-pVXZ-F12 basis sets should be within reach. Such basis sets should be numerically amenable for applications to large molecules due to their lack of uncontracted diffuse functions (of course, diffuse functions will have to be included for computations on anions or Rydberg states).

## 5. Extrapolated Energies

One important aspect of the basis set construction is to investigate whether a given family of basis sets can be used to reliably extrapolate (components of) the energy to the basis set limit. Basis set extrapolation is a standard technique in atomic physics, where partial wave expansions suggest the appropriate extrapolation formula. In molecular calculations, basis set extrapolation is more empirical and relies on the systematic structure of the basis set series. Dunning's work on correlation consistent basis sets instantly spurred a flurry of developments in basis set extrapolation techniques. Several formulas for extrapolation of the correlation energy exist: the work of Helgaker et al., who suggested the use of inverse cubic extrapolation formula.<sup>4,39</sup> This formula suggests that the complete basis set limit correlation energy can be obtained as a linear combination of the correlation energies obtained with cc-basis sets  $X$  and  $Y$ :

$$E_{\text{corr}}^{\infty} = \frac{X^3 E_{\text{corr}}^{(X)} - Y^3 E_{\text{corr}}^{(Y)}}{X^3 - Y^3} \quad (1)$$

Truhlar pointed out that for practical computational chemistry applications, usually at most  $X = 2$  and  $Y = 3$  is feasible.<sup>40</sup> For these low cardinal numbers, the cc-bases do not reliably obey the asymptotic law, and hence Truhlar has investigated a more flexible form:

$$E_{\text{corr}}^{\infty} = \frac{X^{\beta} E_{\text{corr}}^{(X)} - Y^{\beta} E_{\text{corr}}^{(Y)}}{X^{\beta} - Y^{\beta}} \quad (2)$$

and determined the optimum exponent  $\beta$  to be 2.4 for the combination of cc-pVDZ, cc-pVTZ, and CCSD or CCSD(T) from calculations on Ne, HF, and H<sub>2</sub>O. Truhlar's approach was later shown by Schwenke<sup>41</sup> to be a special case of a general approach that approximates the CBS limit energy as a linear combination of energies computed with  $X$ ,  $Y$ ,  $Z$ , etc. basis sets; coefficients in the linear expansion are specific to each method (SCF, CCSD, etc.) and each set of basis sets. For two basis sets, eq 2 can be rewritten in Schwenke's form:<sup>41</sup>

$$\begin{aligned} E_{\text{corr}}^{(\cdot)} &= \frac{X^{\beta} E_{\text{corr}}^{(X)} - Y^{\beta} E_{\text{corr}}^{(Y)}}{X^{\beta} - Y^{\beta}} = \frac{X^{\beta} E_{\text{corr}}^{(X)} - Y^{\beta} E_{\text{corr}}^{(X)} + Y^{\beta} (E_{\text{corr}}^{(X)} - E_{\text{corr}}^{(Y)})}{X^{\beta} - Y^{\beta}} \\ &= E_{\text{corr}}^{(X)} + \frac{Y^{\beta}}{X^{\beta} - Y^{\beta}} (E_{\text{corr}}^{(X)} - E_{\text{corr}}^{(Y)}) = E_{\text{corr}}^{(X)} + f(X, Y) (E_{\text{corr}}^{(X)} - E_{\text{corr}}^{(Y)}) \end{aligned} \quad (3)$$

Hence there is a 1:1 correspondence between exponent  $\beta$  and the unknown linear coefficient  $f(X, Y)$ . We have followed this recipe by using eq 2 and reoptimized the exponent  $\beta$  for each pair of basis sets that was investigated.

Perhaps surprisingly, the extrapolation of the SCF energy appears to be more difficult than the extrapolation of the correlation energy. Halkier et al.<sup>43</sup> established that exponential extrapolation—as long pursued by Feller<sup>44,45</sup>—is more successful than the power law used by Truhlar. More recently, Petersson and co-workers have studied the problem in detail and have used<sup>46</sup> an extrapolation of the form:

$$E_{\text{SCF}}^{(X)} = E_{\text{SCF}}^{(\infty)} + A \exp(-\alpha \sqrt{X}) \quad (4)$$

(the equation is attributed to Karton and Martin<sup>47</sup>). For their new basis sets ( $n\text{ZaP}$ ), the constant  $\alpha = 6.3$  was found to be universally valid. We have followed Petersson and co-workers but have fitted  $\alpha$  to each pair of basis sets used for extrapolation.

Thus, in the extrapolation study, we have fitted one parameter to the SCF energies and one parameter to the correlation energies to minimize the total mean unsigned error for the 21-molecule test set; the optimal values of parameters are given in Table 3. Qualitatively, extrapolations that lead to  $\beta = 3$  and a relatively small  $\alpha$  are preferred. Under these circumstances, the correlation energy extrapolation is thought to be most physically sound, and the less steep SCF energy extrapolation is expected to be more robust in actual applications.

Among the 2/3 extrapolations, the rcc-pV(D/T)Z pair slightly outperforms the other basis sets of the same size, and only cc-pV(D/T)Z comes close. Hence, the use of contracted polarization functions does appear to improve the quality of at least the lower member of the cc-basis set family. Nevertheless, the differences between the various basis sets are not large and amount to about 0.5 mEh in the total energy on average. Augmentation of the ANO basis sets does improve the results, and with ano-pV(D/T)Z+, the mean unsigned error of the extrapolated total energy of 1.27 mEh must be considered as an excellent result. It is, in our opinion, impressive that with such a simple extrapolation scheme one can compute the reference energy with an average unsigned error of less than 2 mEh. In particular, the error in the SCF energy can be reduced to below 1 mEh using the extrapolation formula of Petersson and co-workers, while the Truhlar–Schwenke extrapolation provides correlation energies within 2–3 mEh from the reference values. The results lend credence to Truhlar's choice of  $\beta = 2.46$ . All extrapolations with the 2/3 pairs come close to this value.

All 3/4 extrapolations reduce the SCF error to 0.1–0.4 mEh, with the best results being obtained with the def2 basis sets. However, pc- $n$ , ano-pVXZ, sano-pVXZ+, rcc-pVXZ, and cc-pVXZ are all similarly good. The extrapolation of

**Table 3.** Errors of the Extrapolated SCF and Correlation Energies Relative to the Reference Data (in mEh where Applicable)

	2/3 extrapolation					3/4 extrapolation				
	$\alpha_{23}$	$\beta_{23}$	MUE( $E_{\text{HF}}$ )	MUE( $E_{\text{C}}$ )	MUE( $E_{\text{tot}}$ )	$\alpha_{34}$	$\beta_{34}$	MUE( $E_{\text{HF}}$ )	MUE( $E_{\text{C}}$ )	MUE( $E_{\text{tot}}$ )
cc-pVXZ	4.42	2.46	0.61	2.00	1.77	5.46	3.05	0.22	0.60	0.75
aug-cc-pVXZ	4.30	2.51	0.65	2.06	1.86	5.79	3.05	0.17	0.53	0.68
pc- <i>n</i>	7.02	2.01	0.90	2.69	2.76	9.78	4.09	0.17	0.41	0.28
def2	10.39	2.40	0.47	2.10	2.01	7.88	2.97	0.10	0.66	0.67
ano-pVXZ	5.41	2.43	0.72	2.84	2.20	4.48	2.97	0.18	0.62	0.64
sano-pVXZ+	5.48	2.21	0.32	1.86	1.68	4.18	2.83	0.11	0.28	0.32
ano-pVXZ+	5.12	2.41	0.20	1.29	1.27	5.00	2.52	0.09	0.31	0.38
acc-pVXZ	4.80	2.34	0.85	1.61	1.81	4.92	2.94	0.36	1.17	1.29
rcc-pVXZ	4.43	2.47	0.69	1.82	1.44	5.46	3.00	0.17	0.56	0.72
Roos-ANO	5.15	2.50	0.41	2.19	2.22					

the Roos-ANO with the NASA-AMES set is not fair and has therefore been omitted from Table 3. Pleasingly, all 3/4 extrapolations (except the one for pc-*n*) come up with an optimum  $\beta$  that is close to the preferred value of 3. Hence, for all intents and purposes, it could be replaced by just 3 once one proceeds beyond the 2/3 extrapolation level. In any event, the extrapolated 3/4 energies almost all fall within 1 mEh of the reference values, which is considered pleasing. From this perspective, the choice of the particular 3/4 set might not be overly important and could be done under consideration of computational convenience. In particular, the results demonstrate that the def2-TZVPP/def2-QZVPP pair is well suitable for extrapolation, and the pc-2/pc-3 result is even one of the best in the test set. We do, however, view the latter result with some reservation due to the unphysical exponent of 4.09 in the correlation energy extrapolation, the steep SCF exponent, and a large amount of error cancellation between the errors in the SCF and correlation energy extrapolations. In terms of the SCF extrapolation, the ANO basis sets lead to the least steep extrapolation and may therefore be preferred.

## 6. Comparison of Extrapolation and Explicit Correlation

Despite the impressive improvement of correlation energy due to the use of explicitly correlated methods, the total R12 energies obtained with ano-pVTZ and aug-cc-pVTZ basis sets are approximately 3.5 times less accurate than the corresponding 2/3 extrapolated values. The corresponding quadruple- $\zeta$  ratio is approximately 4. However, at this level, the errors are so small that they probably fall within the error bar of the reference data itself that was “only” obtained through 5/6 extrapolation. The use of cc-pVXZ-F12 basis sets optimized specifically for explicitly correlated methods improves the comparison in favor of R12 methods, but nevertheless, extrapolated energies are more accurate by a factor of 3. The comparison with ano-pVXZ+ is most favorable to the R12 calculations: they are only a factor of 2–2.5 worse than the extrapolated results. Thus, at present, the R12 methods are not competitive with extrapolation for the total energies. However, one can, of course, combine R12 methods with extrapolation, as already pursued by Hill et al.<sup>48</sup>

It would be imprudent to overly generalize these findings. Our past experience with extrapolation methods suggests that their spectacular performance for total energies does not

transfer intact when applied to relative energies.<sup>48</sup> This is particularly evident from the fact that the extrapolated correlation energies may either overshoot or undershoot the true correlation energy, while the error in the correlation energies is always positive in the explicitly correlated methods. Although the Hylleraas functional for the R12 correlation energy provides an upper bound to the exact value, in practice, the upper bound property is not guaranteed due to the inexact Hartree–Fock solution and various approximations involved in R12 methods. The violations are, however, small, and with the modern R12 methods, the basis set limit of energy is approached from above (the basis set error is positive). A more complete and fair comparison of the extrapolation methods vs R12 methods will involve the construction of ANO-type basis sets specifically optimized for R12 methods, and application to relative energies of interest to chemists (reaction energies, activation barriers). This study is outside the scope of this work.

## 7. Computational Details

All calculations reported in this work were carried out with a development version of the ORCA program package;<sup>49</sup> the MPQC (<http://www.mpgc.org/mpqc-snapshot-html/index.html>, accessed July 11th, 2010) and Psi3 (<http://www.psicode.org/index.html>, accessed July 11th, 2010) packages were used for all explicitly correlated calculations. Geometries were optimized with the B3LYP functional<sup>50–52</sup> in conjunction with the def2-TZVP<sup>53</sup> basis set. The geometrical parameters thus obtained are (atomic units and degrees): H<sub>2</sub> ( $R = 1.406421$ ), BH<sub>3</sub> ( $R_{\text{BH}} = 1.1898$ ,  $D_{3h}$ ), CH<sub>4</sub> ( $R_{\text{CH}} = 2.05898$ ,  $T_d$ ), NH<sub>3</sub> ( $R_{\text{NH}} = 1.91599$ ,  $\text{H–N–H} = 107.312^\circ$ ,  $\text{H–N–H–H} = 115.067^\circ$ ), H<sub>2</sub>O ( $R_{\text{OH}} = 1.81975$ ,  $\text{H–O–H} = 105.237^\circ$ ), FH ( $R = 1.747475$ ), B<sub>2</sub> ( $R = 3.661983$ ), BC ( $R = 2.554910$ ), BN ( $R = 2.491487$ ), BO ( $R = 2.272142$ ), BF ( $R = 2.390700$ ), C<sub>2</sub> ( $R = 2.357244$ ), CN ( $R = 2.319042$ ), CO ( $R = 2.126086$ ), CF ( $R = 2.410890$ ), N<sub>2</sub> ( $R = 2.061850$ ), NO ( $R = 2.164009$ ), NF ( $R = 2.491128$ ), O<sub>2</sub> ( $R = 2.276277$ ), OF ( $R = 2.550064$ ), F<sub>2</sub> ( $R = 2.639683$ ). Coupled cluster CCSD(T) calculations were performed with the 1s orbital kept frozen (except for hydrogen, of course). Open shell species were treated in the unrestricted formalism and without restrictions on the spatial part of the wave function.

Explicitly correlated CCSD(T) computations on closed-shell molecules were performed with the CCSD(T)<sub>R12</sub> method of Valeev et al.<sup>26,54,55</sup> The geminal amplitudes were fixed at the values determined by the first-order cusp conditions.



Three- and four-electron integrals were approximated using the CABS+ approach<sup>56</sup> with the uncontracted cc-pV6Z basis as the auxiliary basis set. The standard R12/C approximation<sup>57</sup> was used throughout to approximate the so-called B intermediate of the R12 theory. Exponential (Slater-type) correlation factor  $e^{-\gamma r_{12}}$  fitted to six Gaussian geminals was used in all calculations; geminal exponent  $\gamma = 1.4 a_0$  was used in all calculations except those involving the cc-pVXZ-F12 basis sets,<sup>58</sup> for which the recommended geminal exponents were used. The R12 correction of the CCSD(T)<sub>R12</sub> method was computed using robust density fitting (DF);<sup>42</sup> the following {orbital, density-fitting} basis set combinations were used: {ano-pVXZ, aug-cc-pV6Z-RI (C. Hättig, University of Bochum, Germany, unpublished)}, {cc-pVXZ, cc-pV(X+1)Z-RI},<sup>59,60</sup> {aug-cc-pVXZ, aug-cc-pV(X+1)Z-RI}, and {cc-pVXZ-F12, cc-pV(X+1)Z-RI}. Total energies reported in the rightmost column of Table 2 also include the second-order energy correction from single excitations to the CABS manifold correction.<sup>26</sup>

Atomic calculations were performed with uncontracted Gaussian basis sets as described in the main body of the paper. Calculations were tightly converged on the atomic ground states: He(<sup>1</sup>S), B(<sup>2</sup>P), C(<sup>3</sup>P), N(<sup>4</sup>S), O(<sup>3</sup>P), F(<sup>2</sup>P), and Ne (<sup>1</sup>S). MR-ACPF calculations were performed on top of the CASSCF states using all configurations in the CAS including those of the wrong symmetry or with an insufficient number of open-shell orbitals as references. No contraction or selection of the interacting space was employed, and the calculations were converged to  $10^{-12}$  Eh. The first order density was constructed and diagonalized in order to obtain atomic natural orbital contractions.

## 8. Conclusions

In this work, basis set construction strategies for correlated calculations on molecules were investigated. In particular, it was studied whether the family of correlation consistent basis sets could possibly be improved by incorporating elements of atomic natural orbital construction in their design. The answer to this question is positive: ANO basis sets deliver—provided they are derived from a sufficiently accurate set of primitive Gaussians—much better SCF and slightly better correlation energies than correlation consistent basis sets. The replacement of the uncontracted polarization functions with the contracted ANO ones (rcc-pVXZ) yields a significant but still somewhat limited improvement in the calculated correlation energies, while replacing the s and p parts of the cc-bases with their ANO counterparts (acc-pVXZ) does improve the SCF energies but not the correlation energy. Thus, one seems to be well advised to keep the full ANO contractions in order to obtain the best results at a given basis set size. This also is the most consistent strategy if algorithms can be devised to obtain the integrals over generally contracted basis sets efficiently for larger molecules. This will be discussed elsewhere.

A significant finding of the present study is the large increase in the accuracy of the SCF energies if one only supplements the ano-pVXZ with the next set of valence functions (saug-pVXZ). The increase in the number of basis functions by four per heavy atom is already limited at the

DZ level (19 instead of 15 basis functions) and very small for the higher members of the basis set family. Since the integrals over all primitive members of the underlying set must be calculated anyway, the increase in computation time cannot be overly disturbing once the computational procedure is highly optimized. The full augmentation with the next set of polarization functions (ano-pVXZ+) comes at a high computational cost in the correlation energy calculation, while the gains in accuracy appear to be somewhat limited compared to the calculation with the next higher cardinal number.

The gain in accuracy obtained with the ano-pVXZ basis sets relative to their cc-pVXZ parents is considerable at the double- $\zeta$  level, limited but significant at the triple- $\zeta$  level, and more limited for the quadruple- $\zeta$  variant. Indeed, it was particularly the performance of the double- and triple- $\zeta$  cc bases that was the main motivation for the present work. With explicitly correlated R12 methods, the performance of ano-pVXZ+ bases was superior to that of the cc-pVXZ-F12 basis sets of Peterson and co-workers that were specifically optimized for R12 methods. The combination of these compact basis sets lacking numerically troublesome uncontracted diffuse basis functions with explicit correlation and local correlation approaches appears to be a fruitful route toward accurate computational chemistry. The results of Werner and co-workers<sup>61–63</sup> along these lines appear to be very promising.

The situation changes somewhat if the SCF and correlation energies are extrapolated to the basis set limit. In this work, the SCF extrapolation technique recently proposed by Peterson and co-workers has been combined with the correlation energy extrapolation of Truhlar that is based on the work of Helgaker and co-workers as well as Schwenke.<sup>64</sup> One parameter was optimized for the SCF energies and one for the CCSD(T) correlation energy for each pair of basis sets considered. Among the double-/triple- $\zeta$  basis set combinations, the cc-pV(D/T)Z sets were again found to perform best, but all extrapolations lead to total energies within 2.5 mEh of the reference values. Again, augmentation improves the results obtained with the ANO bases. For the triple–quadruple- $\zeta$  basis set extrapolations, the differences between the various basis set combinations become rather small, and one typically reaches better than 1 mEh deviation from the reference values. It is noteworthy that even with basis sets that were optimized for SCF calculations (pc-2/pc-3, def2-TZVPP/def2-QZVPP) one obtains excellent extrapolations to the SCF and CCSD(T) correlation basis set limits. While for the double/triple- $\zeta$  basis set pairs Truhlar's observation<sup>39</sup> that the optimum extrapolation coefficient for the correlation energy is around 2.4 was confirmed, for the triple/quadruple- $\zeta$  basis set pairs, all basis set pairs (except pc-2/pc-3) show optimized exponents close to the theoretically expected values of 3, which is considered pleasing. Recently, Petersson and co-workers have reported an effort toward extrapolation techniques for molecular calculations and have devised a new series of basis sets. So far, they have published results for SCF energies<sup>40</sup> and more recently also for MP2.<sup>46</sup> It will be interesting to compare these results with the ones that have been obtained in this work once they become publically available.

Having realized the superior accuracy of ano-pVXZ sets compared to segmented bases, it is necessary to develop computational algorithms that ease the burden of integral evaluation. Most integral programs take little advantage of contraction, and the cost of integral evaluation increases with the fourth power of the contraction depth. This clearly leads to extremely expensive calculations for the deeply contracted ano-pVXZ basis sets. Thus, unless procedures that are specifically targeted toward ANO contraction are employed, the use of the ano-pVXZ or any other ANO basis in routine molecular calculations is not attractive. Such techniques have been developed in the framework of the ORCA program and will be reported elsewhere. For a long time, the MOLCAS package has also been optimized for this task, as is amply documented by the many successful molecular applications on the basis of the Lund group ANO basis sets. We do not claim great superiority of our ANO sets over the ones initially constructed by Almlöf and Taylor<sup>19–21</sup> or by Roos and co-workers.<sup>21,22,65</sup> The emphasis of the present work was the comparison between various basis set construction strategies with the main result that the ANO construction scheme appears to be the most successful one if only the number of basis functions but not the contraction depth is of concern. An efficient implementation of an ANO-based SCF and coupled cluster program within the ORCA package will be described elsewhere.

The various ANO basis sets discussed in this paper have been constructed from H–Ar and will be provided to the public via the EMSL basis set library and the Supporting Information of this manuscript. We expect that for first row transition metals, the basis sets designed by Roos and co-workers can safely be combined with the ano-pVXZ series.

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**Supporting Information Available:** Listing of the proposed basis sets. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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